Development of the Sliding Spark Technique for Trace Analytical Spectroscopy of Dielectric Solid Matrices

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Abstract

A novel direct solid-state emission spectroanalytical method based on the pulsed sliding spark source has been developed. The technique is characterised by a radiative transient discharge plasma propagating along the surface of a dielectric solid matrix enforced between a pair of electrodes in air at atmospheric pressure, where matrix excitation is driven by plasma-particle interaction based on geometry- and source opto-electric-modulated electron impact excitation.

This dissertation embodies the results of the systematic theoretical and experimental study of the sliding spark which aimed at the analytical development of the technique for trace quantitative spectroscopy of the heavy elements embedded in the dielectric matrix surface layers.

The optical emission spectrum, when detected and measured in the λ range 212–511 nm at \approx 0.05 nm spectral resolution using optical fibre transmission in conjunction with a holographic blazed grating CCD spectrometer, was found to be suitable for simultaneous multi-elemental analysis. Investigation of the spectral characteristics of several heavy metals embedded in a variety of dielectric matrices (a boro-silicate simulate, borax, polyvinyl-alcohol, cellulose, teflon, Al-Zr simulate ceramic powder, simulate and River sediment samples) has led to the realisation of an empirical scheme for optimal identification and selection of the optically thin lines that are suitable for trace quantitative analysis. The utility of the lines depends on the element and sample matrix. Use of PVC as a matrix modifier results in increased sensitivity through formation of volatile halides. Comprehensive characterisation of the measured spectra provides empirical evidence to exploit the sliding spark at fast pulse frequency also as an atom source for combined emission, fluorescence, and absorption spectroscopy applicable to the elucidation of structural and molecular information by temporal gating, time-resolved techniques.

Practical approaches found in the search for an appropriate calibration strategy for quantitative analysis include the use of internal standards based on Y and La (added) and Si and C (matrix-derived) spectral lines, which compensate for the differing ablation yield, signal drifts and matrix effects in and between complex matrices. Accurate analytical models have been derived for Mn, Ti, V, Ni, Co, Cu, Cd, Pb, Cr, Al, Fe, Zn, and Hg.

A quantification methodology has been developed based on sediment and as model matrix, which combines high sensitivity and satisfactory reproducibility for Mn, Ti, V, Ni, Co, Cu, Cr, Al, Fe, and Zn. Trace quantitative analysis of dielectric solid matrices by sliding spark spectroscopy is realised in the concentration range from several hundred ppb to thousands of ppm depending on the analyte (and the spectral line utilized) and on the calibration strategy adopted for the quantification. The elemental limits of detection vary from several hundred ppb

to few tens of ppm depending on the element, analysed matrix, spectral line, and calibration method. Qualitative speciation analysis is possible for Mn, V, Pb, Ti, Cu, and Co.

Sliding spark spectroscopy has been validated as a new, simple but robust and versatile technique for the direct trace analysis of complex solid dielectric and refractory matrices with a reproducibility at ≤ 12 %, a precision characterised by a confidence interval of $\pm (0.5-10)$ %, and an accuracy by relative efficiency of $\approx 0-10$ % by the successful analyses of Certified Reference Materials (Stream sediments), sewage sludge, a PVC polymer, an independent XRF laboratory analysis of River Rhine sediment, and by the results of comparative analyses made of the same elements using ICP and XRF (polarised radiation, 3-D Cartesian geometry) techniques.

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Symbols and Acronyms

Boltzmann constant
Capacitance decay constant
Distance from the electrodes to the centre of the discharge plasma column
Driver load impedance
Effective rotational constant of classical harmonic oscillator
Electrical efficiency of the spark source circuit
Electron drift velocity in plasma
Energy stored in the spark source capacitors
Frequency of the emitted radiation from an exited atom
Ionisation energy of atom
Lower energy level of an excited atom
Mean power input into the spark discharge
Mean thermal velocity of the neutrals
Number of electrons in the atom outer shell of atom
Plank's blackbody function
Plasma temperature cooling (decay) time
Rate coefficients for impact excitation resulting in radiation of frequency v
Ratio of the spark circuit capacitance to the peaking capacitance
Refractive index of medium wavelength λ
Sliding spark model simulator function
Sliding spark process simulator function
Sliding spark simulator function
Sliding spark simulator prediction function
Spark discharge current damping ratio
Spark source load impedance
Spectral absorption coefficient at wavelength $\boldsymbol{\lambda}$ corrected for induced emission
Spectral line profile at a given wavelength
Standard deviation
The absorption coefficient at wavelength λ
The optical thickness of a flat layer of plasma
Thickness of base dielectric matrix
Time-resolved measured widths of emission lines
Upper energy level of an excited atom
Variance
Velocity distribution of plasma species
Wave number
Wavelength-dependent emission coefficient

$\Delta\lambda_{FWHM}$	Full width half maximum of the wavelength of an emission line
P(v,r)	Local spectral line broadening profile
ω	Angular frequency
θ	Loss angle
ε	Dielectric field strength of a material
Κ	Gladstone-Dale constant
μ	Partition function
[]	Symbol for the condensed phase
0	Symbol for the gas phase
V_H	Frequency of classical harmonic oscillator
σ_{p}	Plasma channel conductivity
$ ho_p,$	Particle density distribution in the discharge plasma shock wave front
ω_{pe}	Electron plasma angular frequency
σ_{s}	Surface charge density
Α	Einstein transition probability for spontaneous emission
a	Radius of plasma column
Α	Scores matrix
А	Surface channel area of spark discharge plasma
AAS	Atomic absorption spectroscopy
ACE	Alternating conditional expectations
ADC	Analogue digital converter
AES	Atomic emission spectroscopy
AFS	Atomic fluorescence spectroscopy
AMRS	Atomic magneto-optic rotation spectrometry
a _r	Intercept of analytical model function
B	Regression coefficients matrix
b	Slope of analytical model function
BEC	Background equivalent concentration
B_{ij}	Einstein coefficient for absorption/induced transitions between levels i and j
С	Spark source circuit capacitance
c	Velocity of light
CCD	Charge couple devise
CFSS	Coherent forward scattering spectrometry
Ci	Concentration of analyte <i>i</i> in a matrix
CLS	Classical least squares
Cs	Inter-electrode surface capacitance
D	Spark source discharge circuit dissipation factor
d_c	Coulombic correction factor for quantum effect
DC	Dark current

DC-GD-MS	Direct current glow discharge mass spectrometry
DCP	Direct current plasma
DDD	Dynamic disruptive discharge
dl	Integration length of measured line intensity over the line of sight
DSI	Direct sample insertion
Ε	Electric field strength
e	Electron charge
Ε	Residual vector matrix
EEDF	Electron energy distribution function
E _n	Energy eigenvalue
ETA	Electrothermal atomiser
f	Oscillator strength
FWHM	Full width half maxima
g	Statistical weight representing the degeneracy of a given energy state
GD	Glow discharge
GF-AAS	Graphite furnace atomic absorption spectroscopy
h	Plank's constant
Ι	Emission integral line intensity from a given spectral transition
i	Spark circuit current (/general variable representing species energy level)
I_B	intensity of the background
ICP	Inductively coupled plasma
IEC	Inter-element correction
ILS	Inverse least squares
ITFP	Imploding thin film plasma
J	Discharge current density
j	Orbital angular momentum (/ variable representing species energy level)
L	Latent variables matrix
L	Spark source circuit inductance
LA-ICP-MS	Laser ablation inductively couple mass spectrometry
LIBS	Laser-induced breakdown spectroscopy
LIF	Laser induced fluorescence
LOD	Limits of detection
LSE	Local Saha equilibrium
LTE	Local thermal equilibrium
М	Molecular weight of excited species
MARS	Multivariate adaptive regression splines
m _e	Electron mass
MIP	Microwave induced plasma
Δ_{mj}	Sample matrix ablation rate

MLR	Multi-linear regression
MOS	Metal oxide semiconductor
MOSFET	Metal oxide semiconductor field effect conductor
MS	Mass spectrometry
Ν	General variable describing number of statistical events
n	Quantum number
N_0	Number of species in the ground state in a excited system
N_{Ap}	Numerical aperture of optical fibre
N_C	Index of refraction of optical fibre
n _e	Electron density
n _{eff}	Effective quantum number
N_i	The number density of state <i>i</i>
NLPLS	Non-linear partial least squares
n _{Rot}	Rotational quantum number
N_S	Optical fibre cladding of index
N_T	Total number of atoms present in an excited system
n _V	Vibrational quantum number
OLS	Ordinary least squares
Р	Principal components matrix
PCA	Principal component analysis
PCR	Principal component analysis
PDA	Photodiode array
PLS	Partial least squares
PSMS	Plasma source mass spectrometry
PTDS	Photo-thermal deflection spectrometry
q(v)	Normalised distribution of emitted radiation in a specified radial direction
r	General space parameter
R	Spark source circuit resistance
\mathbb{R}^2	Correlation function of least squares fitted regression of y upon x
RF-GD-MS	Radio frequency glow discharge mass spectrometry
RMSEP	Root mean square error of prediction
RR	Ridge regression
RSC	Relative sensitivity coefficients
RSD	Relative standard deviation
Ry	Rydberg constant
S/N	Signal to noise ratio
SA-ICP-AES	Spark ablation inductively coupled atomic emission spectroscopy
SAM	Standard addition method
SBR	Signal to background ratio

SBR	Signal to background ratio
\mathbf{S}_{i}	Sensitivity
SR	Stepwise regression
SS-MS	Spark source mass spectrometry
SSS	Sliding spark spectroscopy
S _{SSE}	RSD of the single spark intensity
t	Duration of the spark discharge events, etc.
Т	Temperature of system
T _e -	Electron temperature
T _{ex}	Excitation temperature
V	Observational volume of a section of plasma
V	Spark source circuit voltage
W	Weight of statistical function
X	Dependent (analyte concentration) variable
X	Sample data matrix
XRF	X-ray fluorescence
у	Independent (instrumental response) variable
Y	Sample data matrix
Z	Nucleus charge
$Z_{e\!f\!f}$	Effective charge of the plasma
α	Blaze angle of holographic blazed grating
λ	Emission spectral wavelength
λ_{f}	Mean free path of the neutrals

1.0 Introduction and Problem Statement

1.1 Trace Spectrochemical Materials Analysis

1.12 Atomic Emission Spectroscopy

Atomic emission spectroscopy (AES) is one of the oldest, well established and most powerful of the instrumental analytical methods available for trace quantitative elemental analysis. It is widely applied in a variety of fields ranging from astronomy through geology to metallurgy. The wide applicability of AES is due to its simplicity, rapidity, accuracy and more importantly recently, due to the easily automated nature of emission spectrochemical analysis.

This has stimulated both the demand and search for new fast, accurate and robust methods for the direct AES measurement and analysis of a host of elements in the various materials.

The growing requirement, for instance, for knowledge of impurity element concentrations at the order of a few parts per million (ppm) and below in the various types of new materials mass-produced in industry, or in environmental applications - where recent promulgation of interstatutory regulations dealing with human exposure to low level chemical hazards (regulatory environmetrics) is fast gaining prominence - amplifies this demand. Rapid and precise trace element analyses of the various matrices are hardly possible without spectroscopy.

1.2 Conductive Solids Analysis

Spectral measurement, thus, is often the method of choice in most trace quantitative analyses. The two most common atomic emission techniques for the direct solid-state analysis of materials, but which are predominantly applicable to conducting matrices, are spark- and arc-emission spectroscopy. These techniques can be applied to over 70 elements, and they demonstrate a high degree of specificity as well as adequate sensitivity for most applications.

Many diverse forms of these discharges are used; these include low-voltage resistor-capacitance (RC) circuits with auxiliary ignited breakdown, high-voltage spark discharges, and, to a small extent nowadays, the high-frequency quarter-wave spark sources [1].

The high voltage spark discharge atomic emission spectroscopy technique particularly has been in use for several decades and remains very effective for bulk conductive solid samples. But for poorly conducting matrices this method has drawbacks, which include poor precision, short dynamic ranges, severe matrix effects, and heuristic quantification analytical models.

With proper matrix matching, inter-element interference may be minimised but not eliminated. The material to be analysed in this case must be powdered and mixed with conducting additives such as graphite or copper in an optimal mixing ratio sufficient to achieve reliable matrix-matched calibration and good sensitivity [1,2] then pressed and shaped appropriately for analysis. Alternatively, the material may either be made into compact electrodes by pressing or it is analysed using auxiliary conducting electrodes [3-6].

1.3 Research Problem

1.31 Non-Conductive Solids Analysis

A consistent theme in analytical atomic spectroscopy currently is the search for improved methods of atomisation for sample matrices in solid form. This development can be observed in industrial, medical, environmental, and geological analyses; the challenge is accompanied by a preference, for analytical methods, which are fast, and neither too expensive nor laborious - the so-called direct solid-state methods [7]. The demand for trace element analyses of non-conductive solids in the above context continuously complicates the problem. The novel utility of the surface spark discharge source is yet to be fully exploited in this regard.

The underlying requirement for all atomic methods of analysis is that the sample matrix be decomposed to the greatest extent possible into its constituent atoms. And the atomisation should ideally be quantitative, i.e., preferably without residual bonding in the gas-phase matrix cloud – otherwise that would mean incomplete atomisation, which could lead to changes in the fraction of atomisation from sample-to-sample or from sample-to-standard. It is less important that complete atomisation be achieved than fractional atomisation be consistent; otherwise errors are introduced in the system calibration whose effect is to lower the analytical sensitivity. To the extent that these conditions are not met, analytical atomic spectrometry becomes extremely complicated by the so-called matrix effects.

Because many matrices occur naturally in solid form, for most analyses chemical pre-treatment is usually used to convert the samples into solution. In principle, samples in liquid form are relatively easier to handle, and they readily lend themselves to automation. Solutions also permit relatively simple and straightforward background correction by the use of a solvent or reagent blank. Extra constituents can also be spiked easily to the sample solutions in standard additions or in internal standardisation calibration methods. In order to overcome the problem of matrix effects observed in the spectrochemical analysis of most solid materials, particularly those that especially emit rich optical spectra, a number of techniques have been developed for isolating the analyte from the complex solid matrices; these include, e.g. co-precipitation [8-10], complex formation [11,12], hydride generation [12,13], adsorption [12-14], ion exchange [12,15] and chromatography [12-17].

However, these methods, even the most acclaimed, in spite of their excellent sensitivity, are not without some undesirable ramifications with regard to their applications to accurate solid matrix analysis. The solution methods are concomitant with the risk of contamination from the added (often toxic) chemicals and they are tedious, time-consuming, procedures.

Further disadvantages of solution-based atomic spectroscopy techniques include conflicting requirements for the dissolution of the various elements (particularly for refractory materials, which are either insoluble or contain insoluble components), sample destructibility (which is unacceptable in certain environmental applications [18]), substantial time requirements for sample chemical pre-treatment - in some cases, e.g. in the extraction of additives from polymer matrices the process can take hours [19], loss of volatile elements such as Cd, As, Hg and Pb during the heating process, high expenses incurred from the use of high purity reagents, and dilution of the analyte due to solvent. Dilution errors and sample transfer loses can also often arise from the sample handling steps, leading to poor limits of detection [20].

Direct solid-state analysis is desirable; it is characterised by many benefits among them low limits of detection (LOD), small consumption of sample material, simplicity, speed, and the avoidance of the various drawbacks attributable to dissolution spectroscopic methods [21].

Except for laser-based atomic spectrometry, which is but mostly suited to non-bulk matrices, the obstacle to the full exploitation of solid-state spectrochemical analysis is the fundamental difficulty encountered in the analysis of non-conducting materials. Complicated by the uniqueness and wide range of the matrices (most solid matrices in nature are poorly conducting) encountered in practice, the direct analysis of non-conductive solids, for the elements at trace level, is difficult and therefore a priority in analytical methods development.

The extreme properties of refractory materials, for instance, hamper the application of most known direct solid (and even wet chemical) analysis methods. Direct analysis methods are in fact hardly available for the non-conducting materials; most established methods are nearly exclusively used for conductive matrices. Although X-ray fluorescence analysis remains the most popular of the *in situ* techniques applicable to both conductive and non-conductive matrices, the method suffers from poor detection limits for the low atomic number elements and

requires extensive sample preparation in order to reproduce the matrix effects attributable to crystal structure.

These challenges, coupled with the implications of the great demand for high accuracy trace elemental analytical data for materials in industry and environment, necessitates the development of powerful new methods for fast, direct analysis of non-conducting solids. One such method, the focus of the present work, is the new sliding spark spectrometry technique.

1.32 The Sliding Spark Technique

1.321 Pulsed Surface Spark Discharges

Despite numerous advances in the study of pulsed surface discharges for utility in practical devices, many of their basic physical processes are incompletely understood and thus remain unmodelled and fully unexploited in spectrochemical analysis. The spectrochemical utility of discharges with particular characteristics is limited; the little there is has tended to be based on 'what worked before' rather than on a detailed understanding of the discharge physics. In spark-AES, representative sampling remains as less understood, as is representative excitation.

In spite of their complicated spectral physics, self-absorption and line reversals, special varieties of surface spark discharges propagating on dielectrics [22-25] under various conditions possess the potential for trace quantitative elemental analysis in non-conducting matrices and surface layers. Trace analysis is an ubiquitous theme in material characterisation.

Sliding spark spectrometry, based on the ablative atomisation and electron impact excitation by a high voltage pulsed plasma discharge propagating along the surface of a dielectric solid matrix enforced between a pair of electrodes in air at atmospheric pressure and on the detection and spectrochemical analysis of the resulting optical emission, is a new technique proposed recently by Golloch and Seidel [26,27] for the analytical spectroscopy of non-conducting solids and dielectric surface layers. The spectral emission that is excited from the surface layers of the matrix sustaining the discharge plasma spans a broad spectral range and carries elemental and concentration signatures suitable for trace quantitative spectroscopy.

The 'sliding spark' phenomenon was first observed more than fifty years go by Vodoar and Astoin [28] as a radiative nuisance in spectrophotometry. In the initial experiments two copper electrodes were strapped on to a high voltage resistor. Many improvements (Astoin [29], Balloffet and Romand [30], Romand and Balloffet [31,32]) and studies based on them (Freeman [33], Romand [34]) have since followed, but the main construction remains the same, that is, two

electrodes in good mechanical contact with an insulating or semi-insulating material, which has a surface between the electrodes along which the spark can be initiated.

The mechanism responsible for the formation of sliding sparks is still not well understood; it may be assumed that the potential drop in the discharge gap is concentrated in a narrow region, and so a high emission field is constrained to propagate along the surface of the underlying dielectric. The observed breakdown potential of ≤ 10 kV, support the hypothesis that sliding sparks are initiated by a 'sliding' mechanism over the insulator surface.

The sliding spark is the simplest technique of generating a discharge plasma on the surface of a dielectric material. It is in principle a special variety of the pulsed surface plasma specularly discharging on a dielectric surface but at atmospheric pressure and in air.

1.322 Sliding-Spark Mechanism and Properties

In sliding spark spectrometry, the dielectric solid bounds the transient discharge plasma in one dimension, thus affecting the gasdynamic and radiative properties of the surface in a manner that is distinct from the free spark [24], the lichtenberg patterns (which are produced when a low current is driven across a surface discharge in vacuum), and the radio-frequency 'gliding sparks', which develop across the surface of dielectrics in vacuum under conditions where the opposite side of the dielectric is in contact with a conducting substrate, connected to one of the electrodes [22,23; 34-36].

Due to the small cross section of the sliding spark discharge a high electric field potential drop is achieved, which is concentrated, and propagates, in a narrow region along the surface of the solid with a discharge brilliance that is far superior to the free spark operating at the same voltage and current [25,34]. Electrodynamically, the sliding spark corresponds to the critical damping of a pure reactive current waveform discharging through a low-impedance load. This enables short-lived direct current arcs, which develop high power per unit volume of the sample matrix in a relatively uniform field, to proceed at a considerably lower static breakdown voltage, aided by the field perturbations induced by the surface sample microstructure [35]. In free sparks the discharge is highly non-uniform [22].

The evolution of a sliding spark discharge is accompanied by a growth in the conductivity of the plasma channel caused by the change from electron impact, to thermal ionisation, so the plasma is drawn more to the thin layer adjacent and close to the surface of the dielectric substrate: the high electron temperature that is attained (computed herein to be ≈ 17000 K in the plasma core) leads to increased vaporization, high particle and electron density, high current density, high conductivity, high resistance per unit length, and short optical pulse width. The critical factors

which influence the plasma propagation are field emission from the cathode at the dielectric contact, secondary electron emission, atomic desorption and matrix evaporation.

During discharge a transient creeping plasma develops in the evanescent depth of the dielectric sample material; this enables fast, random ablative vaporisation accompanied by atomisation, ionisation and subsequent excitation of optical emission from the elements embedded in the base dielectric matrix surface layers.

The main characteristic that readily adapts the sliding spark technique to non-conductor material analysis is that the discharge can be sustained in air at atmospheric pressure as a grazing plasma bound by the surface of the matrix, which is also the analysis sample.

The plasma column expansion velocity parallel to the surface - which is higher than that perpendicular to it [23] - compels the discharge to become asymmetrical; therefore the matrix surface layers are readily sampled (though at variable electron temperatures) in the ablation.

1.323 Discharge Emission Characteristics

The sliding spark discharge plasma that is created breaks down most of the underlying sample matrix chemical bonds, and atomises many of the constituent elements. Substrate ionisation and excitation occur, mostly due to the plasma erosion and electron impact, and partial interception, respectively, by the substrate, of the thermal radiation from the dense highly ionised plasma, which heats and evolves the matrix components into the discharge plasma.

The probability of atomic excitation depends on the characteristics of the spark discharge, and of the chemical elements such as ionisation potential, cross section of electron impact, vapour pressure, and volatility of the components in the dielectric matrix, among other factors.

The excitation is accompanied by prompt atomic, molecular and ionic spectral emission over a broad range, from soft X-ray to the NIR; most of the radiation results from the early stages of the plasma thermolization, and from electron-ion interaction and recombination. As the plasma cools, broadband emission decays and atomic and ionic lines are emitted as a result of the subsequent relaxation of the excited species in the matrix. It is this characteristic radiation from the matrix elements that is detected and measured in the sliding spark technique.

The UV component of the emitted optical spectrum, when intercepted by the matrix surface layers, is very efficient in the [further] delivery of energy into the matrix, resulting in enhanced emission per unit of pulse of energy. This is because the plasma radiation emitted as a result of the interactions, which ends up into atomic excitation of wavelength shorter than 250 nm (readily

absorbed) corresponds to the work functions of most materials (these lie in the interval between 2-5 eV); this energy is capable of ejecting electrons from the surface of the sample matrix, and thus of providing [extra] seed free charges that not only help to initiate subsequent sliding sparks, but also to maintain the analytical discharge plasma.

Every excited matrix constituent atom and molecule features specific spectral signatures: the spectral lines emitted by free atoms or ions, or the molecules of the excited matrix elements embedded in the matrix and the interference background are all detected simultaneously.

The latter consists of a continuous intense radiation (mostly in the visible regime) initially emitted from the matrix and air, radiation from the discharge environment and electrodes, radiation scattered in the spectrometer, and radiation from molecular bands originating from the reaction products of the air in the electrode gap plasma with the matrix constituents.

1.4 Applied Sliding Spark Spectrometry

Although interest in pulsed dense plasmas has increased in the recent years, research, on transient surface discharge plasmas (undertaken mostly by former Soviet scientists), has focused mostly on the gasdynamic, electrical and radiative physics applicable to the engineering of novel sources for use in low inductance switches, pulsed light sources, optical pumps for intense excimer lasers, and broadband sources of intense UV and VUV radiation [37-41]. Hardly any attention was directed to applied spectrometry based on these sources.

Meanwhile at the Golloch group laboratory the sliding spark technique has been developed and successfully applied for the rapid semi-quantitative sorting of plastics and fire retardant polymers for industrial recycling, based on their spectroscopic signatures. The new sliding spark technique demonstrated the potential for direct quantitative spectrometric analysis of non-conducting solids when incorporated Sn and Zn were detected uniquely in PVC and fire-retardant polymers which contained chlorine, based on chlorine-enhanced atomisation [42].

Although spontaneous atomic and ionic emission is the typical detection method used in sliding spark spectroscopy, mass spectrometry can also in principle be exploited by sampling the material then transporting the effluent to say, an MS set-up, as is done in a closely related technique reported elsewhere [21,22]. This is known as spark source-mass spectrometry (SS-MS), a semi-classical method for the determination of elemental and isotopic composition of non-conductive solids [4].

A spark exciting a solution sprayed into the spark gap produces an analyte emission intensity that is proportional to solute concentration [1]. Similarly, spark-eroded analyte transported to a DC-

or IC-plasma results in spectral emission that is proportional to the analyte concentration in the original bulk sample.

But when both sampling and emission are observed simultaneously from the same spark, as is the case in sliding spark AES, non-linearity, accompanied by deterioration in the spectral line signal intensity, becomes pronounced.

The work reported in this dissertation was conceived on the hypothesis of the observation that species present in wide ranging classes of non-conducting solids and dielectric surface layers at much lower concentrations than was feasible to detect and measure in the pioneering work by Golloch and co-workers [26,27,42] in the analysed plastics, can in principle be excited, detected and measured when the sliding spark discharge plasma is operated in a halogen modifier environment (which is opto-electrically optimised), and when an appropriate analytical methodology including a calibration strategy are developed.

Spark source opto-electric modulation provides a methodological versatility, which allows for matrix-, element-, and analyte spectral line-dependent optimisation, an approach that [also] opens opportunity for application of sliding spark spectrometry in speciation analysis.

1.41 The Sliding Spark Spectrometer

The Golloch sliding spark spectrometer provides the possibility to accomplish these tasks. The random, spark-to-spark temporal evolution of spectral emission that is observed suggests that simultaneous detection is in principle, from a fundamental point of view, preferable.

The task in sliding spark spectrometry is how to generate highly populated excited ionic states, or their free atoms, from the ablated material in the discharge plasma so as to achieve an algorithmic functional relationship (required for quantitative analysis) between the concentration of the analyte species, at trace levels, in the sampled vapour cloud from which the emission is measured, with respect to the original matrix, with high degree of exactitude.

A closely related and equally challenging task is how to [then] isolate the net analyte signal emanating from a trace analyte species, which is detected from the composite radiation (line plus background) that appears in the spectral windows centred on the analyses lines.

Most of these, and associated analytical challenges, have been overcome by exploiting the versatility of the auspicious developments in CCD array detectors [3]. The use of CCDs has provided the possibility to enhance the linear dynamic range of most analyte species signals of interest in the quantitative analysis, to detect signals with low background at room temperature,

to perform multiple line selection after data acquisition, and to cross-check for line overlaps in the complex spectra that are measured, among other benefits [4].

CCDs have a high readout throughput, sufficient resolution, high peak quantum efficiency and significant responsivity over a wide wavelength range (0.1-1100 nm) so that with appropriate computing hardware, direct trace multi-elemental analysis is realisable on reasonably complex matrices. The large number of pixels on each CCD detector enables the simultaneous recording of multiple spectral ranges. The large spectral databases that are acquired simultaneously, in relatively short periods of time, provide the possibility for computed calibration, library comparison, and parameter fitting [3] – these are approaches which can bolster sliding spark spectrometry if accurate analytical models are developed.

1.5 Summary

This dissertation embodies the results of investigating both theoretically and experimentally the sliding spark source as a new analytical technique for the detection, measurement and direct trace quantitative element spectroscopy of solid dielectric materials.

Spectra have been successfully measured on a number of non-conductive matrices: borax, PVC, teflon, polyvinyl alcohol, and cellulose, as test matrix modifiers. The spectra all include in common, analyte lines detected from the trace elements embedded in the matrix.

At trace concentrations of analyte in the underlying base dielectric matrix the sliding spark plasma is essentially optically thin.

Analytically useful spectral lines for the elements Fe, Cr, Ni, Cu, Pb, Cd, Zn, Co, V, Ti, Mn, Al, As and Hg have been detected, identified and measured, and their spectral response functions explored in the PVC polymer embedding these test elements in their oxide form.

Practical approaches for the efficient matrix element atomisation and excitation, instrumental optimisation, sample matrix conditioning, and the search for appropriate calibration strategies for simultaneous trace multi-elemental quantitative analysis have been developed.

Results of applied analyses are presented for both simulated and real sediment matrices, which have been used as a model matrix for a non-conductive environmental analysis sample.

Quantitative analysis is optimum for most element lines in the concentration ranges up to 2000 ppm - higher if non-linear regression analytical models are used in order to make use of the full range of the spectral response function curves derived.

While simultaneous trace element detection and analysis in complex matrices by sliding spark spectrometry by standard addition is plagued by the discharge plasma-related matrix effects, the use of internal standard (with both standard addition and external calibration) are applicable when a halogen polymer is employed as a matrix modifier. In a pure halogen polymer matrix however, all three standard methods of calibration give precise, accurate results for direct determination of trace elements in materials by sliding spark spectroscopy.

Following this introduction a review of the existing analytical schemes for pulsed plasma atomic emission spectrometry, particularly those for solid-state analysis, is given in Chapter II. The emphasis is laid on the perceived research trends toward analysis of dielectric solids.

Chapter III outlines the plasma-matrix interaction mechanisms and resulting matrix sampling in the direct solid analysis with pulsed plasma discharge techniques, emphasising the sliding spark and how these relate to the spectral chemistry in the sliding spark discharge plasma.

The physics of the surface discharge plasma is presented in Chapter IV, correlating gasdynamic, radiative and electrical computational procedures for modelling surface discharge plasma configurations in order to provide a comprehensive basis of the principles that may be exploited for the engineering of new, better excitation sources for analytical spectroscopy. The mathematical principles of analytical laboratory plasmas are outlined, presented for various analytical schemes. Emphasis is laid on performance characteristics for fast time-resolved spectroscopy, the perceived future development of sliding spark technique.

In Chapter V a description of the sliding spark instrumentation is given, including sample preparation, system calibration, and the analysis scheme adopted for (quantitative) spectral line identification and selection. The spectral characteristics of a number of dielectric matrices are presented and discussed in the context of matrix atomisation-excitation efficiency. Results of test measurements for the reliability of the sliding spark technique to perform quantitative analysis, based on the study of its robustness, precision and accuracy, are also presented.

The practical approach to the quantitative analysis is presented in Chapter VI, which includes the rationale for the choice of sediment as a model matrix. PVC polymer, embedding spiked trace elements, is used to examine the characteristics of sliding spark spectra in detail. Numerous spectral responses are explored, on the basis of which the optimal analytical lines are selected and criteria of their use to perform calibration for quantitative analysis examined.

Studies pertaining to trace element atomisation-excitation efficiency based on the examination of the sensitivity performance of various matrix modifiers: PVC, teflon, cellulose, borax, are

reported in Chapter VII together with the optimisation of the methodological approach based on the correlation of spark source parameters, and matrix particle seize, with element- and linespecific signal intensities, including other spectral performance figures of merit in quantitative analysis. A thermodynamical model is adopted in the attempt to explain the observations.

Chapter VIII explores the quantification schemes applicable to sliding spark spectroscopy while dealing with the search for the appropriate calibration strategies utilising sediment as a matrix modifier. An extensive database of analytical models is derived. The results of the investigations are applied to Certified Reference [sediment] materials, River Rhine sediment, PVC polymer powder, and a laboratory sewage sludge standard, for the purpose of method validation, using the multi-signal techniques. The results obtained from an independent laboratory analysis are used advance a basis for the evaluation of the analytical figures of merit of the technique, relative to other spectroscopy techniques analysing solids.

In conclusion in Chapter IX, the salient features of sliding spark spectroscopy, development of the analytical method, its application, and main results which highlight the versatility of the technique in the trace quantitative spectroscopy of dielectric materials, are summarised, followed by an outline of future perspectives - in terms of novel instrumentation, sample matrix conditioning, method development, hyphenation to other techniques, applicability of chemometrics, further theoretical studies, and new algorithms for the quantification software.

2.0 Solid State Atomic Spectrochemical Analysis

2.1 Overview

The existing analytical schemes in atomic spectroscopy are discussed, with special emphasis to solid-state atomic emission spectrometry. Practical analytical approaches highlighting the tendency in direct solid analysis research toward pulsed plasma-source atomic emission [and mass] spectrochemical analysis are then examined in the context of the spectral excitation techniques for the direct analysis of conductive solids including possibility for the dielectrics.

2.2 Analytical Atomic Spectrometry

Over the last several decades, atomic spectrometry has been used in analytical laboratories under various forms (emission, absorption, mass, fluorescence) and with a large number of neutral atom and ion generation and excitation devices: flame, arc, spark, laser, electrothermal atomiser, etc. In the instrumental analysis techniques, particularly those quantitatively measuring trace elements in the various materials and mediums, spectrochemical analysis is easily the preferred method.

2.21 Analytical Methods

The different varieties of the atomic spectrochemical analytical methods include,

- Atomic Emission Spectrometry (AES)
- Atomic Absorption Spectrometry (AAS)
- Atomic Fluorescence Spectrometry (AFS)
- Mass Spectrometry (MS)
- Coherent Forward Scattering Spectrometry (CFSS)
- Photothermal Deflection Spectrometry (PTDS)
- Atomic Magneto-optic Rotation Spectrometry (AMRS)

Among these methods, the most common are Atomic Absorption Spectroscopy (AAS), Atomic Emission Spectroscopy (AES), and Mass Spectrometry (MS).

Analytical atomic spectroscopy as a method for elemental analysis, exploits quantized transitions characteristic of each individual element, mostly in the [easily accessible] ultraviolet, visible, and near-infrared spectral regions, for identification and quantification.

The best atomic analytical technique in specificity is Atomic Fluorescence Spectrometry (AFS). AFS has demonstrated the successful detection of single atoms. In AFS, each atom can in principle be detected many times since it can be excited over and over again: the radiation emitting atom can be re-excited by an additional incident beam of photons, say from a laser.

Although mainly used for solutions, Atomic Absorption Spectroscopy (AAS) is however the most sensitive and practically reliable. AAS can be used for elemental analysis of powders, solutions, foils and wires [43]. With atomic line sources, AAS is generally a single element detection method. Recent advances have been made, to overcome this limitation. In continuum-source AAS continuum sources that extend well into the [important] ultraviolet range are however limited and not widely available. Another problem encountered in AAS is the generation of a broadband spectral background. The background arises from absorption caused by residual molecules or molecular fragments in the atom source and by scattering from smoke and other airborne particulates. It is considered prudent thus to employ some form of background correction, with either a furnace or flame atomiser - for this a number of background correction schemes are available: continuum-source correction, Zeeman correction, and the pulsed hollow cathode continuum-source procedure. But in Graphite Furnace (GF)-AAS, it is necessary to employ a different temperature program for each element.

Better capability for multi-element analytical spectroscopy is given with atomic emission spectrometry, mass spectrometry and coherent forward scattering spectrometry where there are many resonance lines as well as lines of higher excited states including ion lines of the elements altogether available for quantitative analysis.

Mass spectrometry, although usually destructive, provides information about isotopes readily distinguishing one isotope from another while offering the benefit of extraordinarily low background levels.

Atomic emission with arc, laser or spark, is a two-step process involving atomisation, then excitation. (This is as opposed to AAS, which requires only the steady supply of ground state atoms). In a high-temperature flame or plasma, atoms are not only formed extremely efficiently, they also generate more intense atomic emission. Atomic emission is isotropic and occurs from all elements at the same time, providing the possibility to perform simultaneous multi-element analyses by means of a multi-channel detection system, a technique, which measures several photons from each atom simultaneously.

Atomic emission spectroscopy, though primarily used for conductors, is the preferred primary method to develop for the direct trace element analysis of non-conducting solids.
2.22 Analytical Schemes for Atom Formation

The spectral regions utilised in most of the atomic spectroscopy techniques involve valance electronic transitions. For narrow-band characteristic spectra to be generated, each atom must ideally be isolated from all others, so the transitions are not perturbed by neighbouring atoms or by bonding effects. If this requirement is not met, the resulting spectra are representative more of molecules or molecular fragments than of the atoms.

Solutions are the easiest route through which to atomise analysis samples. Once the atoms are in the gas phase, they can be probed by any of the several spectrometric analytical techniques. The typical analytical schemes for the atomisation processes utilised are outlined in Fig. 2.1.





The different solutions can be converted to free atoms in several alternative ways. For instance, in an Electrothermal Atomiser (ETA), a small aliquot of the solvent can first be evaporated from the sample at gradual moderate temperature so any organic material is ashed, then the temperature is increased rapidly to the point where the sample is vaporised and ultimately atomised.

The complexity of most solid samples demands the use of various dissolution procedures ranging from conventional heating systems [44] through microwave-assisted procedures to acid decomposition for each kind of matrix.

One of the most preferable is slurry sampling, which generates very little acid waste, and is less affected by inhomogeneity problems than would be realised in direct solids analysis [45].

A more straightforward means of generating free atoms may be used. Mercury, for example, may be atomised by the chemical reduction of inorganic mercury in solution. Neutral mercury atoms can then be driven from solution simply by passing an appropriate carrier gas through it.

The liberated atoms are present in a relatively cool environment and may be measured alternatively by such techniques as atomic absorption or atomic fluorescence spectrometry.

For certain types of elements, such as tin, antimony and arsenic, a chemical reaction will yield not free atoms but rather volatile species, e.g. stable hydrides, which can then be dissociated at moderate temperatures into free atoms. The volatile hydrides can be driven from solution by bubbles of an appropriate gas, into a moderate-temperature flame or furnace, for atomisation.

Nebulization - probably the most common technique in analytical atomic spectrometry - serves to increase the surface area of the solution sample, so solvent evaporation (desolvation) can proceed more rapidly and the resulting dried solute particles are volatilised better.

Pneumatic nebulization has been commonly used for introduction of liquid samples into analytical systems such as inductively coupled plasma, as well as plasma mass spectrometry.

Once formed, droplets in the nebulized spray are sent into a high-temperature environment such as noble-gas plasma. There, desolvation and solute-particle vaporisation take place, and the resulting vapour is converted into free atoms. The environment in these discharges is often hot and energetic enough that many of the atoms formed wind up as positively charged ions.

2.23 Direct Solid Matrix Atomisation

Naturally, it would be desirable to analyse solid samples directly in their natural state. Techniques and devices exist which attempt these task. Most of the techniques involve particulate formation and subsequent transfer of the generated particles into emission, or mass analysers. In principle, the devises allow [in]direct solid analysis of bulk samples. Several methods have also been developed for the direct introduction of solids into standard analytical systems (e.g. Inductively Coupled Plasma (ICP), the Microwave Induced Plasma (MIP) or Direct Current Plasma (DCP)). These include Direct Sample Insertion (DSI) [46-48], electro-thermal vaporisation [49-51], arcs [52], spark ablation [53], Glow Discharge (GD), Laser Ablation (LA) [46] and slurry (often ultrasonic) nebulization [53] together with the optimisation strategies of these techniques for special sample matrices [54].

Walsh and Russel [55] proposed monitoring sputtered analyte from the solid state in a glow discharge environment by atomic absorption spectrometry as a viable alternative to solution-based AAS methods. The use of glow discharge has increased steadily since. GD produces an almost ideal environment for AAS. Solid sampling atomic absorption methods [56,57] have even been developed for the determination of volatile elements such as Pb, Cd, As Cd, Hg, and Zn, whose analysis can be practically very complicated.

For the determination of very small trace element concentrations the single element method, Solid Sample (SS)-GF-AAS [43, 58-62] is very good. The method however requires high-grade homogeneity of the sample powders, because the sample weights used for calibration and analyses are very small. In this case electrothermal vaporisation [63-65] also provides attractive advantages: improved sensitivity, small sample size. ETV also provides the possibility of separating the analyte from some of the matrix components by using an appropriate temperature-time program before the analyte is transported into the excitation source. ETV is especially a very ideal analytical technique for direct solid spectrometry for trace elements when combined with techniques such as ultrasonic slurry sampling [66-68] or when mounted as ETV-ICP-MS (which is a multi-element method).

But in all these cases stringent requirements are dictated on the properties the particles should have in the analytical form [69]; for the case of plasmas, during the discharge the particle size should be $\leq 1.5 \,\mu\text{m}$ (which is very difficult to achieve in practice), the volatilisation rate should be highly independent of sample matrix, and the composition of volatilised material must equate, with high exactitude, that of the sample being analysed. In slurry injection GF-AAS, for instance, each sample dose applied should contain at least 1000 particles for representative sampling [70,71]; which means if 10 mg sample mass is applied from a uniformly ground state, the particles must take the seize of 14 μ m at the maximum - an expensive, difficult criterion to meet. The techniques are therefore to a large extent constrained by the high mass transfer efficiency required so as to be comparable to "dry" solutions.

2.3 Plasma-Source Atomic Spectroscopy

Plasmas, optically induced in gas phase, were first described by Marker *et al.* [72]. Since then, the majority of studies of these plasmas have been spectroscopic in nature; the utility of various forms of plasmas (Inductively Coupled Plasmas (ICP), Microwave Induced Plasmas (MIP), Direct Current (DC) plasma, AC electrode arc or spark discharges, glow discharges, etc.) for chemical analysis has been known for several decades.

Elemental analysis by plasma-some atomic spectrometry can be performed by atomic emission, atomic absorption, atomic fluorescence or mass spectrometry. In all four cases, the plasma source acts as an atomisation reservoir with simultaneous excitation of both neutral and ionised species.

In the application to elemental analysis by plasma emission spectroscopy, the spectral features desirable for solid analysis depend on the plasma characteristics, which in turn are related to the experimental conditions through the processes of vaporisation of the material and absorption of the plasma radiation. When the plasmas have an annular shape, there is a better interaction between sample and plasma [73].

Plasma source mass spectrometry (PSMS), which includes a number of well established methods (plasma ionisation sources) of elemental analysis of almost any material regardless of the sample form or desired levels of precision, accuracy, and determination, has to a large extent been built on the efforts to develop better methods for direct solid atomisation.

The analytical performance in plasma [mass] atomic spectrometry is strongly dependent on the form and procedure by which the sample is introduced into the plasma discharge. The process involves two steps.

The first is the dispersion of the sample by an appropriate method: ablation or sputtering for solids (nebulization for liquids). The second step consists in the conditioning of the dispersed particles or droplets, which are then carried into the discharge plasma by a flow of gas.

One of the simplest methods of direct elemental analysis of conducting solids is the use of a spark as a sample introduction system for an ICP. The simplicity of spark ablation (SA)-ICP-AES makes this technique even more suitable to a variety of analyses. Many applications have already exploited this technique e.g. [74-78]. The particulates formed by the high-energy

electrical discharge are transported via an argon carrier gas to the ICP, where they undergo atomisation, ionisation and excitation and are detected either by emission or mass spectrometry. The latter, ICP-MS, has excellent detection limits, extended multi-element capability, and suitability for coupling to various sample introduction systems.

Coupled to the ICP-MS, spark ablation is a complementary mode to liquid sampling techniques [79]. The argon plasma source operates at a very high temperature (for the ICP at the MS interface the temperature is of the order of 8000 K). In the ICP-MS however, several analytical pitfalls can jeopardise the accuracy of the analysis when new or relatively unknown matrices are involved; as the fine sample aerosol moves deeper into the plasma, it undergoes several complex processes in turn: vaporisation, atomisation and finally ionisation.

Glow-discharge devices on the other hand have remained mostly applicable to conductive solid samples because of the need to impart a negative charge to the sample surface, in order to attract argon-ions to it. At low pressure, ion bombardment sputtering is an inefficient means of sampling except at frequencies below 1 mHz.

In a glow discharge, ordinarily operated at pressures in the range of 1 Torr, the sample surface is bombarded by energetic noble-gas ions, usually of argon. Through this steady bombardment, the surface is eroded layer-by-layer, a process called "sputtering". Atoms freed from the surface as a function of time are taken from successively deeper layers within the sample. Recording the spectrometric signal as a function of time permits a depth profiling. Nowadays, radio-frequencyglow discharge (RF-GD) modes permit depth-resolved analysis of non-conductive samples as well. Low pressure sampling discharges can be maintained with radio-frequency input as well as with DC input.

2.4 Direct Solid Spectrometry with Pulsed Plasma Sources

Despite the wide use of analytical plasma sources, pulsed plasma AES remains limited in routine applications to sample introduction methods, where they have demonstrated wide utility as solid sampling sources for atomic spectrochemical analysis.

The best established methods in pulsed plasma-source atomic spectrometry employ a glow discharge, dc arc, laser, or high-voltage spark. These techniques are, particularly excellent in providing sampling devices for atomic mass spectrometry. SA-ICP-AES, for instance, is now considered an efficient method for the direct solid analysis of metals and alloys, but the analysis of non-conducting samples is less common.



Fig. 2.2 Schematic design of the SPARK 10 ablation cell [80]

The schematic design of the SPARK 10 ablation cell, illustrated in Fig. 2.2, was described by Webb and co-workers [51] for the analysis of granite-graphite briquettes. The authors published scanning electron micrographs, which indicated that while melting plays a role, the pitted surface morphology of the ablated pellets exhibit textures characteristic of physical ablation. Thus, mechanical ablation may be taken to be the mechanism responsible for the removal of the non-conducting particles [44].

A variety of discharges, including glow discharges, arcs, sparks, plasmas, magneto-plasmas (and an assortment of magnetically compressed and heated discharges), provide the ability to analyse the elemental composition of (mostly conductive) solids without requiring dissolution or other time-consuming sample preparation. The various direct solids analysis techniques are based on emission spectrochemical principles, which are in turn based on, and affected by, the theory and phenomena of pulsed/continuous plasma excitation.

In these devices, the plasma erodes the solid sample, creating free atoms. In the arc, laser, and spark, the atoms are ablated directly from the matrix target (or underlying) surface. In most analytical discharges, there is an additional gaseous species (usually Ar, but at times, N_2 or He) present. (A flow of buffer gas through the discharge can help maintain a constant composition for the bombarding ionic gas). The free atoms are detected either by their spectral emission, or by their ionisation.

Elemental analysis based on the emission from plasma generated by focusing a powerful laser beam on a solid, known as Laser–Induced Breakdown Spectroscopy (LIBS), has been emerging in the recent years. In this technique, the laser is employed not much as an atomisation source as compared to an ablation-based sampling device.

The sample material ablated by the laser can also be fed into any of several spectral sources for further atomisation and excitation. LIBS was first reported in 1962 by Brech [81]. The method has since been applied in only limited number of cases to carbon-based materials [82].

For laser power densities exceeding the breakdown threshold of a material in the focal volume, a plasma characterised by a high excitation temperature and electron density will be initiated. Laser plasmas containing exclusively singly and multiply charged ions are very energetic and homogenous; electron densities and excitation temperatures can reach up to 10^{19} cm⁻³ and 25000 K respectively at the onset of a laser pulse [83].

When the laser is intended primarily as an ablation device, a laser beam (e.g., excimer or an-YAG) ablates a small amount 10-50 μ m spot and produces a cloud of micro particle material, which can then be dynamically transported to e.g., the ICP by a flow of argon gas. The micro particulates are decomposed in the plasma, atomised and ionised prior to being mass-analysed with detection limits in the parts per billion range.

While laser ablation (LA)-ICP-MS requires knowledge of at least one element in the unknown sample to be used as internal standard, the Laser Induced Fluorescence (LIF) spectroscopy technique permits the detection of ground state or long-lived, non-radiative, excited-state atoms, molecules or radicals [84].

The laser technique is not only useful for bulk analysis; as opposed to beam rastering techniques which are more suited to large surface analyses it can also be utilised for determination of the spatial relationships of sample surfaces (zonation) [85] by stationary beam focusing. Unlike the glow discharge, arc or spark, a laser beam can be focused to discrete, extremely small spots on a solid sample surface so that not only depth-resolved but also lateral-resolved quantitative information can be obtained.

While the instrumentation industry has been moving in the direction of lasers and using an ICP for excitation and an array of sources for sampling, most conventional ICP-MS/ES methods are devoted to liquid samples. Consequently in the area of solid analysis the limitations of the technique itself become apparent, so that the single spark source (spark, glow discharge, pinch discharge, etc.) systems will in all likelihood remain the sources of preference in particular niches [5]. Both the spark and the glow discharge spectral sources have already been used for

elemental analysis for decades, with a methodology based on empirical observations. The dominant sampling mechanisms for each of the discharge sources are summarised in Table 2.1.

Discharge	Main sampling mechanism	Additional sampling mechanisms				
DC arc	Thermal (distillation)					
Exploding thin film	Thermal					
Glow discharge	Sputtering	Thermal (at high currents)				
Hollow cathode	sputtering	Spallation				
Discharge		Thermal				
Jet-assisted glow	Thermal (melting)	sputtering				
Discharge						
Magnetron	Thermal	Sputtering				
	(magnetically enhanced)	(magnetically enhanced)				
Spark	Thermal (melting)	Sputtering (from melt)				
Theta pinch	Thermal (?)	Sputtering(?)				

Table 2.1	Dominant same	ling mecha	nisms for co	mmon analytical	discharges [5]	
$1 a \cup 1 \cup 1 \cup 1$	Dominant sam	Jing meena		Jinnon analytical	uischarges [J]	

Variations of the glow discharge technique used for solid sampling include the planar or Grimm glow discharge [86], the hollow cathode discharge [87,88], and the jet-assisted glow discharge [89]. Both emission and mass spectrometric observation of eroded material is common, and absorption [90], or fluorescence [91] measurements are also possible. In the glow discharge setup, while not as dramatic as with atmospheric pressure plasmas, emission intensity from samples species evolves with time [92].

At low pressures, glow discharges have narrower lines and the rate of [sample] surface evolution is slower. Narrower lines do not only reduce problems with interference, they also provide evidence that discharges at low pressures are optically thin, reducing the problem of self-reversal commonly encountered in discharges which sample larger amounts of material. Collision line broadening is minimal, especially in the jet assisted glow discharge. Absorption radiation can also be used for detection. Combined with a continuum source for backlighting [93], very wide dynamic range may in principle be achieved in glow discharges.

Novel glow discharge devices have recently been re-introduced as viable ion sources for direct mass and atomic emission spectroscopy [94]. Cathodic sputtering of non-conductors for analysis by direct-current glow discharge mass spectrometry (DC-GD-MS) is accomplished by

powdering the sample and compacting it with high purity, electrically conducting metal powder, such as Ta, Ag, Cu, or Al [95]. The compacted powder sample is essentially a suspension of non-conducting particles in a 'sea' of metal powder. This approach is used routinely for bulk trace analysis of non-conducting solids; however, it has several limitations.

Direct sputtering of non-conducting solids has been demonstrated in radio-frequency (RF) glow discharge sources [96-98]. However, the signal intensities were shown to be dependent on sample thickness [99-101], with excessive generation of heat, causing sample fracturing during analysis. The RF glow discharge technique was developed in 1993 by Marcus and co-workers [102]. This technique allows non-conducting materials to be analysed directly without mixing them with a conducting matrix. A study of the sputtered surfaces on glow discharge AES using scanning electron microscopy showed that the sputtering process is non-thermal. RF powered glow discharge ionisation sources have since been developed for the bulk- and depth-resolved analysis of metals, insulators and polymers systems alike [97,103]. To the best of the author's knowledge, no sector RF-GD-MS instrumentation is however commercially available to date – one must be assembled in-house. These sources have been interfaced to single [103] and double quadruple mass filters [104,105], quadruple ion traps [106] and the magnetic sector mass analysers [107].



Fig. 2.3 Schematic diagram of ion processes envisioned to occur during the sputtering of non conducting solids with the use of secondary cathode¹

¹ At time t = 0 Ar⁺ ions bombard the surface of the Ta cathode, dislodging Ta atoms, which may either diffuse into the negative glow region, where they are subsequently ionised by a variety of interactions, or plate out onto the surface of the adjacent solid non-conductor. After some time, t = x the sputtered Ta atoms have accumulated to form an electrically conductive film on the surface of the non-conductor. The presence of the conductive film permits the direct sputtering of the non-conductor by incident Ar⁺ ions.

The secondary cathode technique in combination with RF-GD-MS [108], which has already been applied in analysis [109,110], is the latest alternative to the compacted powder approach. Its relatively simple geometry is shown in Fig. 2.3.

A metal cathode with a circular central orifice is attached to the analytical surface of the conductor. The diameter of the cathode is smaller than that of the anode, thus, the region of the metal cathode closest to the non-conducting surface is also sputtered upon initiation of the glow discharge. This technique relies on the re-deposition of sputtered metal atoms onto the surface of the non-conducting sample. Neutral metal atoms liberated from the cathode redeposit to form an electrically conductive thin film on the exposed surface of the non-conducting sample. Sputtered Ta atoms redeposit and continuously replenish the surface film, permitting depth analysis of the under-covering non-conductor.

The DC-carbon arc AES offers numerous benefits for analysis – direct solid analysis, wide element coverage, minimum sample preparation, and preservation of data for extended periods of time (if recorded on photo plates). The vacuum arc has hardly been used for quantitative spectrochemical analysis.



Fig. 2.4 Simplified schematic circuit representation of the arc discharge source

Fundamental studies [111] have revealed that several processes influence the line intensity, namely thermochemical reactions taking place in the graphite cup, and atomisation and excitation processes in the arc plasma. Arcs traditionally distil the electrode material, so that fixed exposure times for all samples give rise to prominent matrix effects. Arcs also tend to be extremely unstable in the wandering of the cathode spot over the analyte electrode, which limits precision. Several approaches, such as modification of the sample matrix by addition of graphite, 'buffers' and carriers, addition of internal standards, and the optimisation of sample preparation protocols, graphite cup geometry and DC operating conditions, have been developed in an attempt to overcome these effects. Background can be minimised by masking the image of the electrodes to cut off the grey body continuum.

Although the thrust of the vacuum arc research is limited by the high currents and voltages that are required to maintain a vacuum arc, if one wishes to perform quantitative analysis of (conductive) solid material there are fewer methods of convenience than DC-arc excitation, photographic detection and micro densitometry, to identify the prominent lines of the elements.

In the exploding film technique, the film, in principle acts as a fuse. Because of its thinness, the film has a significant resistance and the resulting Ohmic heating quickly vaporises the film. At that juncture the structure of the system suddenly changes, as the vaporised film is a gas of free atoms, which are non-conducting. A voltage builds up across the vapour until a plasma is formed. Typically, the plasma forms through metal vapour if the discharge occurs at atmospheric pressure. Once the plasma forms, it grows and heats up not only the metal vapour, but also any particles deposited on the metal, prior to vaporisation. The particles are eroded, and, if they are sufficiently small, consumed. The emission evolves in time and space, with the continuum concentrated close to the surface where the film originally sat, and the signal decays a few cm above the original explosion surface. In general, the thin film species emission lines are self-reversed, but lines from the analyte species are optically thin.

Goldberg and Robinson [112] relatively recently demonstrated a new source suitable for direct solid sampling of refractory materials: the plasma gun. This source is an offshoot of the imploding thin film plasma (ITFP) source [113,114]. The plasma gun segregates spatially the emitting plasma plume from the current-carrying atomisation region, resulting in significantly decreased continuum background emission and minimum absorption of analyte line emission relative to the ITFP emission spectra.

Because plasmas contain ions and electrons whose trajectories can be altered by magnetic fields, only in the absence of an externally imposed magnetic field can magnetic effects on discharges be ignored. Plasmas are diamagnetic, so magnetic fields tend to affect the shape of a plasma before they affect its energies. The direction of a charged particle can be changed by a magnetic field, but not its total energy. The purpose of utilising magnetised plasma devices is to confine the plasma to stimulate more intimate contact between the plasma and sample in the bid to obtain improved spectrochemical performance.

In the theta pinch, current circulates around the discharge. The magnetic field lines run parallel to the discharge axis. A pulsating magnetic field, which is created by the discharge current produces a current sheath, which creates a magnetic pressure gradient. The resulting magnetic compression and subsequent heating lead to temperatures between 100-500 eV in a typical sub-Torr hydrogen plasma, which is sufficient enough to sample even refractory solid.

In the Z-pinch, on the other hand, a cylindrical shell of current is obtained either by creating a cylindrical pull of gas which is then ionised, or by imploding a thin metallic film. The current runs parallel to the discharge axis so that the magnetic field lines circulate about the discharge axis. Magnetic compression results, and an intense continuum is produced. The analyte sits inside initial current sheet, and so it is surrounded by hot plasma, which vaporises it.

Although work on low pressure operation of magnetron sources [116] suggests that powders might also be analysed using this particular method, magnetron sources have been, till to date, mostly employed not for solids but for analysing solution residues deposited on graphite.



Fig. 2.5 Simplified schematic circuit representation of the [free] spark source

The most widely used device in instrumental analysis is perhaps the high voltage spark source. A spark source is a plasma, which is enforced by sufficient voltages between a pair of electrodes. The low resistance provided by plasma allows a propagating injection current. Typical peak currents range from 30-1000 A, with many commercial instruments operating as low as 100 A. The cathodic electrode is eroded during periods when the current increases: at these times, there is a significant continuum produced in the cathode space charge region. While current decreases, continuum dissipates, and good signal-to-background ratios can be obtained for neutral species emission lines. A simplified circuit diagram for the commonly used spark is shown in Fig. 2.5.

The direct application of conventional spark AES to non-conducting samples is not possible however. Analyte sampling and excitation mechanisms in sparks are still poorly understood as a result of the complex nature of the analytical spark discharges. The non-linearity of analyte working curves in the spark discharges has been the subject of numerous investigations [117-120]. These investigations have been hampered by the convoluted process of analyte sampling and excitation upon which the transient plasma behaviour is superimposed. Only heuristic methods for analyte and matrix specific have been developed to deal with such non-linearity.

Extensive information on the electrical and physical characteristics of the surface spark discharge variety relevant to spectroanalytical performance are also reported in the literature. Most of the work has however sought to exploit the surface spark as a production source of beams of positive ions for subsequent trace analysis by mass spectrometry [6,35].

The phenomenon known as 'sliding spark' was reported over fifty years ago. While investigating vacuum sparks at the High Pressure Laboratory of the CNRS, it was found [28] that the use of a 'sliding spark' - where both electrodes were in contact with a material of poor conductivity - provides sufficient reproducibility for absorption spectrophotometry.

The pioneering electrode geometry for this new variety of the surface discharge are discussed elsewhere [34], including their use in absorption spectrophotometry in the extreme ultraviolet spectral regime. Then, the very property that is exploited in the work reported in this dissertation – the appearance of detectable and measurable spectral lines from the underlying base matrix – were an inconvenience for the intended application. Romand [34] has reported a three-electrode configuration in which he attempted to avoid the reported problem.

The analytical applications accomplished included the development of a commercial direct reading apparatus for the detection of selected elements in metals chiefly in steel, which were made with this source utilising the line spectrum emitted by highly ionised atoms, using those lines that arise from s-p transitions in ions having only one or two outer shell electron(s).

Surface spark discharges propagating on dielectrics [22-25] thus possess the potential for quantitative elemental analysis in non-conducting matrices, in spite of their complicated spectral physics. The RF spark discharge plasma in vacuum developing across the surface of dielectrics has been called, on the other hand, a 'gliding spark'.

The gliding discharge [22,23; 34-36] is a particular variety of the surface discharge that takes place between two electrodes across the surface of a dielectric material under conditions where the opposite side of a dielectric sample is in contact with a conducting substrate, which is connected to one of the electrodes - a very significant difference with the sliding spark source described in this dissertation. The specific configuration of the electrodes (Fig. 2.6) in gliding sparks strengthens the electric filed over the surface of the sample, creating optimum conditions for the sputtering and ionisation of the material for the direct injection into a mass spectrometer.

The difficulties in the direct analysis of non-conducting materials by [free, including gliding] spark sources may be overcome by using the sliding spark. Sliding spark spectroscopy, the technique that is the subject of this dissertation, is a special variety of the pulsed plasma specularly discharging on a dielectric surface at atmospheric pressure in air (Fig. 2.7).



Fig. 2.6 The schematics of gliding spark geometry



Fig. 2.7 A simple schematic view for the sliding spark discharge source

A transient creeping plasma develops in the evanescent depth of the dielectric surface, which enables fast ablation, vaporisation, atomisation, ionisation and subsequent spectral radiation emission from the elements embedded in the matrix. The sliding spark technique is a potentially powerful method for the direct excitation and quantitative detection of trace elements in nonconducting and poorly conducting solids and surface layers if both the basic physics and spectrochemistry of the discharge are investigated, modelled and understood in order to be utilised in developing accurate appropriate analytical methodology schemes.

III

3.0 Sliding Spark Plasma–Matrix Interaction Mechanisms

3.1 Introduction

In the field of pulsed plasma analytical discharges, the feedback between sample erosion and plasma behaviour has only been studied to a limited degree to allow reliable modulation of sampling in quantitative sliding spark analysis, based on solid knowledge of thermochemistry. Notably absent from the literature are the effects of sample heterogeneity and microgeometry. Most amorphous solids are agglomerations of micro-size grains, with varying compositions at the grain boundaries than in the bulk of the grain. Pulsed discharge plasmas may selectively erode the grain edges, or the low melting point materials preferentially, or they may attack the high points on the matrix surface due to the strong electric field around a conducting point. Further, previously molten material (or element), which has dissolved substrate matrix, may also be preferentially sampled. Although in low current discharges such topographical features may be less prominent, assorted complex microstructures have been observed [121].



Fig. 3.1 Plasma-matrix interactions and discharge generation in the sliding spark¹

Pfender [122] and Ecker [123] have discussed in significant detail energy exchange and mass transport process between particulates and flowing plasmas but which may be of some relevance to explaining matrix particle dynamics encountered in sliding spark spectroscopy sampling. In

¹ Electrodynamically, the sliding spark discharge plasma is a space charge of dielectric strength ε_p at the boundary of two mediums – air, characterised by ε_{air} , and the sample matrix of strength ε_s – interacting dynamically with the sampling volume (interface) in the matrix.

this chapter, simple micro particle thermodynamics is combined with insight from plasmamaterial interaction in the various practical schemes in an attempt to assemble a representative picture of plasma-matrix interactions in the sliding spark, which are relevant to those processes that are critical to method development for trace quantitative analysis.

3.2 Plasma-Matrix Surface Interaction

The spatial extent of the space charge in a pulsed plasma is inversely related to the discharge pressure. At atmospheric pressure, it may be less than 0.1 mm thick in diameter, where as at pressures of the order of 1 Torr, it may be 5 mm thick. The energy density in the discharge plasma varies significantly. Except within the space charge, over 97 % of the current (particularly in low pressure plasmas) is carried by electrons. Energy is extracted from the electrons into the heavier species within the space charge and ionisation zones. The analytical characteristic of a discharge plasma adjacent to a matrix is integral to the sampling process.

In high electric fields, the matrix surface may additionally emit electrons due to field emission. In general, however fields of several gigavolts per meter are required to realise such emission. Thermionic emission would thus be expected to be more common in the sliding spark discharge. The emitted electrons are easily accelerated by moderate electric fields, and they can induce plasma deformation above the matrix surface, whereby the plasma thus formed can enhance the heating of the surface through both ion and electron impact.

When an ion generated in the sliding spark discharge plasma impacts on a solid matrix surface, it is neutralised. This [contact] neutralisation liberates energy in the amount equivalent to the ion's kinetic energy plus its ionisation energy. If the neutralised atom rebounds from the surface, some of the kinetic energy is retained in the environment phase surrounding the sample matrix. The ablated atom always has less kinetic energy than the incident ion. Even at low energies, much of the kinetic energy of ion impact is transferred to the solid substrates.

The effect of matrix specific chemistry is a critical factor. Preferential erosion of matrices that are chemically reactive towards the discharge environment (reactivity is a function of moisture content, concentration of the dominant gas, and the temperature) may be anticipated. Since melting point is also function of sample composition, a very complicated particle dynamics situation is set up in typical sliding spark quantitative analysis sampling scheme.

3.3 Sampling Mechanisms

Plasma sampling of solids in general may be divided into three classes: sputtering, thermal phenomena and chemical phenomena. Thermal phenomenon may further be categorised into bulk heating, melting, vaporisation, particulate formation, and differential dissolution.

In the sliding spark discharge, sputtering is limited because the conditions that favour it are applicable mostly for low pressure situations or discharges in vacuum, so all three cases of thermal sampling must be considered to contribute more to the matrix sampling to varying degrees of extent. The partial pressure of an initially sputtered analyte, even to a limited degree is enough to produce a plasma in which non-sputtering sampling mechanisms dominate the near-surface behaviour of the matrix. A sliding spark thus ideally samples both by sputtering and by bulk heating. Sampling efficiency, defined as mass of sample ablated per unit energy dissipated in the discharge, is both matrix- and environment-dependent.

Another process that may be relevant in sliding sparks is reactive ion etching, which involves chemical bond formation. A specific ion or neutral species resident in the discharge plasma disrupts the matrix sample surface structure, loosening the bonds between surface atoms and the bulk material, which leads to the formation of free atoms, molecules or radicals, many of which are detected in the spectroscopic dynamics of the particular discharge (see Chapter V).

The hard part in the atomisation scheme of the sliding spark is fixed sampling of matrix material. Energy transport and differential dissolution make it impossible for ablation to give accurate sampling. The shorter the input energy pulse, the closer to ideal will be the sampling, as the input energy will be concentrated into a smaller volume, closer to the surface, causing more localised heating than will a longer energy pulse, which leads to sufficient plasma channel spreading.

Generation of isolated atoms from condensed matter is poorly understood, especially when the plasma environment is maintained at a pressure above 1 Torr, as in the sliding spark.

As the typical voltage across analytical discharges exceeds the sputtering threshold, sputtering in principle should be a major source of free atom production. Sputtering may be caused by a variety of mechanisms. Just at the moment of discharge ignition for a sliding spark, there may be sufficient electric field strength to momentarily give plasma ions enough energy to individually cause underlying matrix sputtering to occur. An ion with sufficient energy can disrupt the bonding of surface atoms sufficiently to break the atoms free from the solid, ejecting them into the environment above the solid. But this occurs only when ion energy is above 100 eV [124], and quantum yield (atoms removed per incident ion) is less than 1 until the energy is several hundred eV.

At pressures of from about 30 mTorr, where the mean free paths of the matrix particles in the plasma are short compared to the size of the average analytical discharge, only the make-up of the environment in the region adjacent to the cathode is relevant to sampling. At high (including atmospheric) pressures, the mean [plasma] ion energy decreases to less than the voltage imposed on the discharge (thus limiting the number of high energy plasma ions impinging on the matrix surface), and collisions convert much of the energy of individually accelerated ions into heat, i.e., lower energy of a large number of neutral and ionised species, which reduces sputtering but increases the importance of heating mechanisms.

The portion of the plasma species with kinetic energy less than 2-3 eV transfers energy to the matrix surface inefficiently. For this cool regime, the plasma can be regarded as a thermal bath, and the heating can be described by the normal equations of thermodynamics. When energy disposition due to heating is sufficient, ion sputtering is replaced by sublimation or boiling as the principle means of sampling.

All energy fluxes have a strong non-linearity dependence on a variety of factors, not least of which is temperature, in which a pulsed plasma is changing based on the rate of energy deposition at the surface. Thermodynamics thus places constraints on what processes are possible in sampling the matrix. Such commonly known constraints are Ohmic laws, thermal conductivity and heat capacity of the plasma, the work function of the matrix surface atoms, melting point, boiling point, thermal conductivity, heat capacity, and surface tension - all of which are each a function of the make-up of the material subjected to the plasma erosion

For instance, thermal conductivity by the bulk material tends to cool the sample surface by diffusing the incident energy through the bulk. The rate of energy conduction from the point of heating is proportional to the temperature gradient. Approximating the spark core plasmas as a point source of heat, temperature gradient will fall as r^{-2} as one moves into the bulk, where *r* is the distance from the point of heating in a typical analysis. The temperature gradient and subsequent sampling depth will vary from one material to another, including between the same bunches of analysis samples.

On the other hand vaporisation and melting rates are known to be inversely proportional to the enthalpies of the thermal processes. At sufficiently high currents (for a given matrix, sample uptake is proportional to $\int i dt$ of the spark current waveform, where *i* is the current driven through the sample surface discharge defined by the plasma channel, and *t* is the ablation time [1]) the heat flux to the sample matrix surface will exceed the ability of that surface to conduct heat to the bulk material without rising significantly in temperature. Resistive heating of the matrix is usually small compared to the energy liberated at the plasma-sample interface by the

other mechanisms involved in the discharge process. At higher discharge plasma energies, one must assume total transfer of energy from the plasma to the matrix surface. Collective sampling phenomena then become important.

The solid surface providing ions to a plasma 'heats' up until the combination of radiative cooling, conductive cooling, electron emission, and material evaporation balances the thermal load of ion bombardment, neutral species bombardment, and photo-absorption is realised. If at this point the sample matrix species have significant vapour pressure, sampling will occur.

3.4 Particle Vaporisation and Atomisation

An ideal quantitative elemental analysis sampling scheme in the sliding spark, regardless of whether it is based on pulsed plasma sputtering or thermal ablation, would need to remove a fixed volume of sample, atomise all the material removed, and excite it to a well-defined temperature under local thermal equilibrium conditions. In that case, any particulates entering the discharge plasma would need to be completely vaporised; the best requirement for this to happen sufficiently quickly is that all the atoms should 'see' the same environment at the moment of vaporisation.

Further, the plasma effecting the atomisation must in principle remain in contact with the eroded material long enough to vaporise any particulate matter in it; so, the liquid material left on the sample surface during the sparking process must be quenched rapidly enough to prevent dissolution to a significant degree.

Generally there is re-solidification of molten analyte at the end of each discharge. This may be ignored for continuous discharges in which the post-discharge portion is an insignificant fraction of the total experimental time. But in sliding spark discharges, re-solidification alters the matrix surface prior to the successive discharges: for pulsed discharges, the sampled matrix spot is allowed to cool and solidify periodically.

The kinetics of the cooling has a profound effect on both microstructure and matrix composition as multiple ablation proceeds. Positionally unstable discharges may act as intermittent discharges at various positions on the matrix surface until the specimen is totally molten. In this regard, the pulsed nature of the sliding spark is already a nearly ideal design than would be the case for a continuous discharge source, since the matrix surface re-solidifies periodically before much dissolution has occurred. If a high frequency circuit were used for the sliding spark, to prevent the problem of differential dissolution, much higher energy (but low current) pulses would be needed to ensure a more energetic plasma where ion bombardment from the plasma removes the analyte via spallation other than bulk heating. Differential sensitivity in the sliding spark is however difficult to "instrument" against since it arises mostly from differences in momentum transfer cross-section of the atoms when elements of different atomic weights are subjected to bombardment in the matrix surface.

Although the vapour propagation and fate of sampled material following matrix ablation are difficult to predict in terms of the trajectories taken by free atoms once they have been produced, if one is sampling briquetted powders, as is the case in the work reported in this dissertation, much of the vaporisation goes on in the bulk plasma core rather than at the matrix sample surface.

To vaporise a particle in the sliding spark, it must be heated sufficiently so that the vapour pressure of its constituent elements results in free atom formation. This does not necessarily correspond to reaching the boiling point of the matrix material. The critical parameters are the discharge plasma temperature and discharge frequency. If the residence time of the particle in the plasma is short, as in high frequency scans, plasma temperatures in the excess of boiling point may be necessary to transfer sufficient heat in the matrix surface to cause vaporisation in the short time. This is easily achieved in the present sliding spark source however because it reaches ~17000 K (seer Chapter IV) and the maximum discharge frequency achievable is 50 Hz, i.e., 25 ms scan time, which is long enough on the scale of typical analytical discharges. With a long residence time, even a vapour pressure less than the ambient pressure will result in the atomisation of the matrix particles in the discharge plasma.

For small matrix particles, the entire particle is at the same temperature, (i.e., the thermal conductivity of both the particle is comparable to the heat flux). In such a case [5],

$$D_o - D = kt \tag{2.1}$$

Representative atomisation will thus be more critically dependent on the temperature realised in the sliding spark discharge than it does on particle size of the matrix ablated into the discharge plasma. It has been found that particle diameters much above 30 μ m cannot be universally vaporised. For large particles, the surface and bulk temperatures differ, in which case,

$$D_o^2 - D^2 = kt. (2.2)$$

where

 D_o = initial particle diameter (cm);

- D = particle diameter (cm) at some time *t* (the diameter changes due to discharge collisions);
- k = rate constant, which is a function of temperature, heat capacity of particle, and thermal conductivity of particle and plasma (cm²s⁻¹).

IV

4.0 Discharge Plasma Generation and Radiative Characterisation

4.1 Overview

The experimental study of the characteristics of air plasmas at atmospheric pressure has been gaining importance in both theoretical and industrial applications, including in the context of spectrochemical analysis. Simple designs for these plasmas may be tailored for possible use as plasma reactors, as light sources, for thin film deposition or surface modification of materials, and as plasma ramparts without resorting to high vacuum systems, using air - due to its low cost, abundance, and favourable physico-chemical properties (chemical reactivity, simple thermodynamics, etc.) - either as an energy carrier or as a chemically reactive medium.

Despite the extensive information available on the electrical and physical characteristics of grazing discharges a good picture of the sliding spark discharge process - particularly, that which permits sensitive spectroanalytical applications - is not yet available. This is in contrast to the free spark discharge, which has been in use for trace analysis of conductive matrices.

Little is known about the distribution of the ionised and excited elements in the sliding spark discharge, the lifetimes of the surrounding atoms especially the ions in discharges operating at high frequency, the mechanisms by which these species give rise to different plasma temperatures, or by which they are removed from the plasma column.

Complex molecules and radicals including CN and other polyatomic species are formed in the air sliding sparks (numerous molecular bands appear in the measured spectra), but little is yet known about the reaction mechanisms that produce them.

Substantial study, modelling and simulation are necessary, therefore, the long term goal of which should be to clarify the spectrophysical characteristics of the sliding spark source which, besides generating engineering applications from the resulting models, may further understanding of the energetics between the discharge plasma and sample matrix; this is important both in formulating sampling and in the modulation of the atomic excitation.

In order to optimise the optoelectronic characteristics of the sliding spark for applied spectrometry, an understanding of the physics of the discharge as a function of the experimental conditions is required.

For instance, to compute the population densities and to reproduce the energy exchange of levels for the excited species of a dense atmospheric air plasma one must take into account the varied collisional and radiative mechanisms involved; this calls for resorting to a statistical mixture of independent particles approximation for the atoms, combined with a semi-analytical mathematical description of the energy level properties [125,126].

This chapter deals with the physics of the sliding spark discharge, focusing on those plasma energetics that can provide the analytical tools necessary for the engineering and application of the spark source in robust quantitative spectrometry.

4.2 Gap Breakdown and Plasma Channel Development

Surface discharges are inherently low impedance, i.e., $< 1\Omega$ loads. Sparks driven by low inductance circuits were first comprehensively investigated by Andreev *et al.* [127]. In a conventional capacitor-discharge, the discharge circuit typically consists of passive circuit elements: inductance *L*, capacitance *C*, and resistive elements *R*, in series with a spark gap whose resistance may be denoted by R_g . A small inductance *L* (~ 170 µH) in the circuit permits a short optical pulse width of the order of a few µs with a fast optical rise time (~ 1.2 µs) [41]. Electrodynamically, the sliding spark corresponds to the critical damping of a pure reactive current pulse discharging through a low-impedance load. An instantaneous voltage pulse, V_i , is developed at the cathode immediately the potential drops across the electrodes, leading to a sharp inhomogeneous electric field strength, *E*, which possesses a large normal component E_{\perp} (due to the presence of an [equivalent] inter-electrode surface capacitance C_s) just before the streamer initiation mode. E_{\perp} is related to the surface charge density, σ_s , by [24].

$$E_{\perp} = 4\pi\sigma_s = 4\pi V_i C_s \tag{4.1}$$

Most of the voltage drop occurs near the electrodes. V_i depends on the dielectric strength of the base material used and on its surface structure, the field in-homogeneity (especially at the sample-cathode contact interface), and on the voltage pulse duration [128]. Upon discharge initiation, the gap voltage increases quadratically, while the gap impedance simultaneously rapidly decreases, within nanoseconds, to a fraction of an Ohm until the moment of breakdown - normally at ~ 27 kV/cm in dry air (for free discharges and less for sliding sparks). For a given substrate and gas environment, $V_i \propto C_s^{-\gamma}$, where the parameter γ is less than unity for most dielectric materials sustaining the discharge in air at atmospheric pressure.

For the special case of a solid dielectric bound to a rear-surface ground plate (see Fig. 2.6), $C_s = \varepsilon \Delta$, where Δ , and ε are the thickness dielectric strength of the dielectric material respectively.

Hence, as opposed to free sparks, electrical discharges across materials with large dielectric permittivity proceed at characteristically much lower breakdown voltages.

Due to the smaller cross section of the sliding spark discharges a higher electric field potential drop is realised; this develops a high power per unit volume concentrated in a narrow region along the surface of the dielectric. This enables the short-lived direct current arcs, which are formed initially, to proceed at a considerably lower static breakdown voltage in a relatively uniform field aided by field perturbations induced by the surface microstructure [22,35], resulting in discharge brilliance that is superior to the free spark operating at the same conditions [25,34].

Impact ionisation of the air adjacent to the surface of the underlying dielectric sample matrix nearest to the electrode at first produces a weak pre-discharge streamer, which begins to propagate along the sample surface towards the anode as a narrow inter-electrode filament. Before breakdown, streamer production is immediately followed by attachment of the electrons to the neutral particles in the region nearest to the electrode. The presence of a strong electric field makes the ionisation process predominant. The electric field accelerates the free charged particles, which undergo ionising collisions with the air molecules in the vicinity, generating more electrons and positive ions. The kinetic energy of the charged particles is partly transmitted to the surrounding neutral particles through random collisions, leading to a heat transfer from the charged particles to the neutrals. The zone of strong ionisation, initially occupies a volume smaller than the luminous channel. Completion of the discharge circuit then produces current flow in the form of a cylindrical plasma channel, having properties analogous to the free spark, just above the sample surface in which collisions between drifting ions and electrons in the plasma and the atoms in the dielectric matrix surface layers are involved in high energy excitational momentum transfer.

Radiation emitted by the discharge plasma rapidly heats up and vaporises the elements in the surface layers of the sample. The radiative plasma that produces spectral excitation in the wavelength range 620-250 nm corresponds to the work functions of most materials (2–5 eV), so this radiation ejects electrons from the surface of the sample matrix, providing the seed free charges that [further] maintain the plasma. The UV component of the excited spectrum, which is intercepted by the sample matrix is especially very efficient in the delivery of energy into the matrix surface layers, resulting in enhanced excitation per unit of pulse energy delivered into the discharge gap. The vaporised species from the sample modify the gasdynamic and radiative behaviour of the analytical gap. The breakdown has then progressed into a fully developed sliding spark discharge plasma. The plasma column that is formed expands radially symmetrically over the surface during the discharge duration with a velocity parallel to the surface which is higher than that perpendicular to it [23]. The critical factors which influence the

plasma propagation are field emission from the cathode at the cathode-dielectric contact, secondary electron emission, atomic desorption from the sample, and matrix evaporation. The sliding spark discharge is highly transient, spatially heterogeneous, microscopically irreproducible, and discrete in the type of radiation emitted down to times less than fractions of a microsecond both with respect to plasma channel and to the electrode vapour.



Fig. 4.1 Planar geometry and spectrometer image positions for the spectroscopic studies [5]

The evolution of the sliding spark discharge is accompanied by a growth in the conductivity of the plasma channel caused by the change from electron impact to thermal ionisation, so the plasma is drawn more to the thin layer adjacent and close to the surface of the dielectric substrate. A high electron temperature (*ca* 16500 K) is attained in the core of the grazing plasma, which leads to increased vaporisation, higher particle and electron density, high current density, higher plasma conductivity, and high resistance per unit length - all these phenomena permit fast spectrochemical excitation of the sample via surface fragmentation, vaporisation, ionisation and excitation in the discharge plasma column. The plasma channel conductivity σ_p , and electron density n_e , are related by the well-known expression $\sigma_p = J/E = ev_d n_e/E$, where J is the current density, *E* is the field strength, and v_d is the plasma electron drift velocity. Because of the large values of n_e and J in surface spark discharges as compared to unconfined discharges, channel conductivity is [also] characteristically larger in the sliding spark.

When the discharge plasma is fully developed, n_e can be approximately be described as cylindrically symmetric. There are a variety of methods to measure n_e . Mathematically, an approximate solution of the Abel integral from the plasma distribution yields [24,129]

$$\eta^{2} = 1 - (\omega_{pe} / \omega)^{2} = 1 - 3.18 \times 10^{9} n_{e} / \omega^{2}$$
(4.2)

where η is the real component index of refraction of the plasma to a probe (diagnostic) light, and ω_{pe} and ω are the electron plasma and probe light angular frequencies respectively. The

measurement technique that yields Eqn. 4.2 exploits the fact that the discharge shockwave sound (acoustic signal) that accompanies the sliding spark breakdown propagates through the plasma and perturbs the index of refraction of the plasma medium thereby degenerating optical homogeneity. The shock wave velocity in the plasma channel may be inferred from transit time measurements made using a miniature quartz piezoelectric gauge. A sharp change in the refractive index along the discharge section has been observed [40]. Due to the presence of an 'electronic gas'–like medium when the plasma is fully developed the index drops to less than unity. The shock wave occurs delayed at above 80 μ s [131].

Upon discharge initiation after 2 μ s when the ionisation and luminous zones coincide, a shock front perpendicular to the surface rapidly separates from the luminous channel at a velocity of ~ 1000 ms⁻¹. The radially converging shock wave detaches from the expanding radiative plasma and travels through the unperturbed surrounding air medium. A photochemical wave component (currently being exploited for inversion and lasing in surface discharge–driven excimer and gas lasers) travels ahead of the shock wave, and, depending upon the prevailing physical conditions, may or may not detach from the shock wave.

The shock wave itself and the gasdynamics of the discharge are related to the opto-electrical parameters of the spark source, hence the wave's potential for utility in background correction. Line transitions from vaporised electrode and substrate species within the high temperature plasma channel's core are normally absorbed by the cooler vaporised particles travelling with the expanding shockwave front. This explains the time dependent reversal of, for instance, the Al I line at 308.215 nm and the variations in the calculated electron temperature.

The particle density distribution, ρ_p , in the shock wave front, where the temperature is unlikely to exceed 4000 K and the air is weakly ionised, can be obtained from the empirical relation $\eta - 1 = K \rho_p$ for $\eta > 1$, where *K* is the Gladstone-Dale constant.

The discharge gap electrodynamics of the sliding spark can best be understood by equating a fast repetition rate, high voltage dc spark source to an alternating current spark unit. Once the gap has broken down, the discharge proceeds independently of the charging circuit and is dependent only on the values of *C*, *L*, and *R*, and upon the voltage V_c to which the capacitor is charged at the time of breakdown.

Neglecting the gap resistance, the current, *i*, passing through the gap is given by

$$i = \left(V_c \sqrt{C/L}\right) \left(e^{-\frac{Rt}{2L}}\right) \frac{\sin t}{\sqrt{CL}}$$
(4.3)

where *t* is the time after gap breakdown.

The sliding spark can thus in principle be considered as a time-dependent, purely resistive load $R_s(t)$, having negligible self-inductance and self-capacitance. From Fig. 4.2, the total spark source circuit inductance is given by

$$L = L_c + L_\ell \tag{4.4}$$

where L_{ℓ} is the transmission line self-inductance, and L_c is the loss inductance. The selfcapacitance for the transmission line and switchgear may be neglected.



Fig. 4.2 Equivalent circuit of (a) a pulsed surface–spark discharge employing capacitive energy storage [5] and (b) the sliding spark source circuit employed in the measurements¹

The equivalent loss resistance of the capacitor (which is used to store the discharge energy) is given by

$$R_c = D\sqrt{L/C} \tag{4.5}$$

¹ The ignition and charging circuits are separated from one another by the diodes d1, d2.

where R_c is the loss resistance of the capacitor; D is the circuit dissipation factor defined by $D = \tan \theta = \varepsilon_i / \varepsilon_r$, where θ is the loss angle and ε_i and ε_r are the imaginary and real components of the dielectric permittivity of the sample substrate.

In oscillations circuit theory, Eqn. 4.3 holds only for $R^2/4L^2 < 1/LC$. If $R^2/4L^2 = 1/LC$, the circuit current is critically damped and no oscillation occurs; while if $R^2/4L^2 > 1/LC$, the circuit current is over-damped and just as in the critically damped case, only a single pulse of current is realised. The sliding spark source circuit is tailored to ensure critical damping.

Table 4.1The discharge control parameters of the sliding spark source

Electrical

- Capacitance of the energy storage capacitors
- Circuit inductance
- Charging voltage
- Electrical circuit efficiency
- Pulse repetition rate (= sample ablation frequency)
- Maximum peak current
- Peak current pulse width
- Observation time constant

Mechanical

- Substrate (sample matrix) composition
- Electrode material/composition
- Sample matrix surface structure
- Inter-electrode gap distance
- Electrode geometry

Environmental

- Gas composition
- Gas pressure
- Ambient moisture content
- Ambient temperature

The electrical efficiency η_{el} of the excitation source circuit defines the efficiency with which the energy stored in the capacitors ($E_s = 0.5 CV_c^2$) is deposited in the gap, and is expressed as

$$\eta_{el} = \frac{\int i^2(t) R_s(t) dt}{\int i^2(t) [R_s(t) + R_c + R_\ell] dt}$$
(4.6)

 η_{el} is a function of the external resistance R_{ext} (total circuit resistance minus surface discharge load resistance R_{sd}), C_s , V_c , the type of gas atmosphere employed in the discharge together with its pressure, and the source geometry. R_{ℓ} can be chosen to be small, while R_c may be minimised by either employing low resistance in the circuit or by selecting low inductance, low-loss capacitors. Because of the low impedance of the load, the discharge efficiency also depends sensitively on external loses such as the characteristic loss resistance of the capacitors and on the transmission line resistance.

A practical limit can be imposed on the initial rate of change of the maximum current attained in the source with time i.e., di_o/dt (= V_c/L) in order to control the source discharge strength ('hardness' or 'softness') which determines the power input into the discharge plasma channel. The time, $t(i_p)$, at which the maximum current is observed increases with increasing *C* and decreases with decreasing *L*, in accordance with circuit theory:

$$t(i_p) = 0.5\pi \left(LC\right)^{\frac{1}{2}}$$
(4.7)

The functional dependence of the peak current i_p can be derived from elementary circuit analysis; it is given by

$$i_p = V_c \sqrt{C/L} \exp\left(-\pi\xi/Z\right), \xi^2 \ll 1$$
(4.8)

where $\xi = R / 2\sqrt{L/C}$, the current damping ratio.

Under the conditions of critical damping, the discharge changes from oscillatory to almost aperiodic. This condition can be attained for small values of energy liberated per unit length of the discharge gap because the resistance of the spark channel in the arc stage of the surface discharge is low.



Fig. 4.3 Typical optoelectric characteristics of the sliding spark spectrometer source

A peaking capacitor C_p can be [optionally] used in the circuit to increase the current and optical rise time at the load: the presence of a peaking capacitor induces a voltage on the analysis sample (load), which is larger than the charging voltage V_c . The peak voltage on the peaking capacitors V_p occurs approximately at the time $t(V_p) = 0.5\pi\sqrt{LC}$, which can explicitly be derived thus

$$\frac{V_p}{V_c} = \beta (2 - \pi \xi) / (\beta + 1) \tag{4.9}$$

where β is the ratio of the circuit capacitance C/C_p . At the moment of breakdown it may be assumed that the surface discharge load $R_{sd} = \infty$ until $t = t(V_p)$.

 V_c/L together with η_{el} strongly influence discharge channel expansion velocity and therefore the rate of channel spreading, which is related to the surface sampling efficiency. In surface sparks η_{el} is inherently high since the resistance per unit length of spark gap is significantly larger than it is in free sparks operating at the same conditions, hence high luminance, high n_e , J, σ are realised. The luminous intensity reaches a maximum simultaneously with the excitation current. At maximum discharge luminescence, the evaporation rate of the ablated sample material is proportional to the rate of change of the discharge current [25]. In general, the conditions that ensure the most rapid liberation of energy into the spark channel are: almost all the energy stored in the capacitors before the discharge be released in the initial stage of the discharge, and the initiated discharge should stop when the resistance of the spark channel becomes significantly less than the resistance for critical damping $R_{cr} = 2\sqrt{L/C}$. The impedance condition for critical damping of a current waveform is $Z_d = 0.5Z_s$, where Z_d, Z_s , are the driving and spark source load impedances respectively. Z_s can be taken to be the minimum circuit resistance load, i.e., $Z_s = R_s(t)|_{min}$. Z_d , which is equal to $\sqrt{\frac{L}{C}}$, is the practical condition required to maximise the mean power input, \wp_d , into the discharge load; the latter is expressed as

$$\wp_d = \frac{1}{t_d} \int_0^{t_d} i^2(t) R_s(t) dt$$
(4.10)

where t_d is the duration of the discharge. A specific electric energy E_d is dissipated per unit time per unit surface area A of surface channel for a non-oscillatory circuit, i.e., a critically damped or over-damped current waveform. The low inductance increases the peak current density and the rate of energy deposition since

$$i_0(t) = 0.368V_c\sqrt{C/L} \tag{4.11}$$

The initial rate of the current rise (Fig. 4.3) is almost independent of the type of discharge ($\xi < 1$ - under-damped), ($\xi = 1$ - critically damped), ($\xi > 1$ - over-damped). In Eqn. 4.3 the first term gives approximately the peak current for low damping, second term the damping, while the third term represents the oscillations.

When the spark current ceases, the plasma ion density and temperature begin to decay. The cooling (decay) time, τ , can be deduced from kinetic theory according to the relation [130].

$$\tau = \sim 10^{-1} \ell_d^{-2} / \upsilon \lambda_f \tag{4.12}$$

where v and λ_f are the mean thermal velocity and mean free path of the neutrals respectively, while ℓ_d is the distance from the electrodes to the centre of the discharge plasma column. A similar time can be defined for the diffusive loss of ions to the electrodes and into sample surface layers. A small degree of plasma relaxation in the form of electron/ion recombination occurs for approximately 75 % of the discharge lifetime. In sliding spark spectrometry thus one must aim at engineering an excitation source to maximise the η_{el} (for maximum \wp_d , $Z_d = 0.5Z_s$; for maximum η_{el} , $R_c + R_\ell \rightarrow 0.$), shorten the optical pulse width, and increase the emission luminous intensity for the source circuit parameters used, which must also be tailored to enhance radiation in the spectral region of interest. Radiative enhancement in a particular spectral region can be effected by choosing a substrate matrix binder for the sample whose species readily ionise in the discharge plasma and subsequently radiate via line transitions in the region of interest.

4.21 Approaches to Model and Simulate the Sliding Spark

The gasdynamic and radiative behaviour, together with the interactions between the discharge plasma produced by the sliding spark source and the sample, require several approximations if they have to be analytically tractable. Studies, which couple understanding of chemistry and physics in the control of the discharge properties, are key to this goal. In non-local thermodynamic equilibrium plasmas operating in air at atmospheric pressure, radiative transfer and non-stationary atomic states must especially be considered, time-resolved spectral studies are necessary, so are comparisons of experimentally observed properties with known theoretical formalisms of the spectral emission.

To understand the energy transfer from the source into the analytical gap, and how the atomisation, ionisation and excitation of samples initially present as solids evolves into the discharge gap, simulation is necessary. Plasma model simulations can considerably simplify the physics of the sliding spark by enabling one to take into account a variety of factors affecting the spectral line emission, and their characterisation, detection and measurement.

A global model for the system can in be realistically deduced which would allow a simulation of the non-linear behaviour of the sliding spark discharge as a function of current, voltage, time, etc., including sufficient realism to account for more mechanically useful information such as discharge stability, spatial and temporal temperature and electron and ion density profiles, and geometrical confinement.

Although emphasis on this tasks is not the main thrust of the work presented in this dissertation in the meantime, at least two practical approaches to further the understanding of the fundamentals of sliding spark spectrometry as a new analytical technique have been identified:

 Macroscopic properties of the discharge plasma may be studied and the thermodynamics modelled, the results of which can then be used to explain the discharge radiative behaviour. • Microscopic mechanisms can be investigated in the attempt to determine specific sampling and excitation pathways in the discharge plasma, which will furnish knowledge relevant to excitation, and to the modulation of time- and spatially-resolved quantitative spectrometry.

The first approach consists of a theoretical examination of the spark source electrical network possibilities including the discharge circuit and gap. Some idealisations could be used, considering related experiences from previous research made on free spark discharges. Agreement between simulation and observation for free surface sparks could only be obtained by postulating a gap discharge capacitance in the vicinity of 0.001 μ F, which corresponds to the capacitance of a gap shunt diode waveform [133]. The gap, without the analysis sample adjacent to it, has traditionally been simulated as a shunt capacitance during the breakdown face. This yields a rather complicated system of differential equations, which require some simplifying assumptions in order to be solved.

The thyratron may be modelled as a small specifiable resistance when on, and as an infinite impedance when reverse-biased. Source diodes can be modelled as a small resistance when forward-biased, and as a capacitor shunted by a large resistance when reverse-biased. The plasma resistance, which together with the discharge current determine the energy input (and therefore energy transfer into the surface layers of the analysis sample) in the case of the sliding spark may be considered to be that of a fully ionised plasma, i.e., one whose electric conductivity is determined by electron/ion collision rather than by collisions involving neutrals. For this assumption to be valid, the plasma should be > 0.1 % ionised; for one atmosphere plasma in air this requires a minimum electron density of $\approx 2 \times 10^{16}$ cm⁻³.

The second approach could consist of experimentally studying the approximate functional dependencies, including the time evolution of the sample-gap dynamics, followed by deriving the necessary mathematical relationships with subsequent experimental verification [132]. The rapid heating of electrons and the matrix sample atoms in the sliding spark discharge plasma column leave the sample atoms in an under-ionised state relative to the steady-state for the typical electron temperatures that are observed. Thus, the plasma populations are transient and require a time-dependent treatment.

Possibilities for immediate study include an examination of the time behaviour in the discharge, where the primary current electrons are important. In addition, power balance calculations could be performed to predict local plasma conditions over the entire plasma channel as shown in Fig. 4.1. Codes would be generated, which can be used to study the cooling plasma after the discharge current has been damped and the line radiative characteristics of the discharge predominate. Measurement of the emitted radiation can be compared to calculations to provide plasma diagnostics and additional confidence in the computational models. The models can also

be extended to provide support for laser-based and other related pulsed discharges in gases/air at atmospheric and higher pressures. The strong overlap of the electronic charge cloud of the sample constituents in the plasma demands on the other hand a fully quantum mechanical treatment - at least for the electrons since the model should not fail to include such mechanisms as breaking and forming of molecular bonds, ionising of the various species, and the recombining of free electrons, which are apparent from the nature of the measured spectra (see Chapter VI).

In the first instance possible models include considering the sliding spark gap, adjacent to which there is an underlying dielectric sample matrix, as dynamic fixed resistor; this resistor can be allowed to remain constant over short (~ ns) computation time intervals, then 'forced' to evolve after a successive point has been computed, or it can be approximated as being inversely proportional to the excitation current. The simulation can then be approached as an initial value problem – a problem where the initial conditions of the system are known, and one desires to compute the time evolution of the system's behaviour. To account for the drastic non-Ohmic drop in the space charge near the electrodes one may have to assume that a fixed voltage drop occurs in addition to some Ohmic losses. Spectral line-dependent DDD (dynamic disruptive discharge) breakdown voltages for the various measured lines become simulation parameters, to be obtained by observing breakdown voltage progressions for a given gap width and ablation repetition frequency. The spark gap can be modelled as a peaking capacitor of specific value, and a constant resistor after breakdown. Indeed the gap behaves as a capacitor before breakdown.

The explicit resistance of the gap due to the 'memory effect' ionisation from previous sparks must be accounted for – it may be modelled as constituting a resistance in parallel with the intrinsic gap resistance. If one assumes a model in which impulse ionisation at breakdown is followed by recombination, the impedance would grow exponentially with time, tending to damp the discharge more quickly than would a pseudo discharge in an appropriately seized resistor. Strict linear damping ($R \propto i$) has been shown to be a useful model [133]; this model accounts for changes in impedance as the diameter of the discharge changes in direct proportion to the discharge current. Impedance is indeed dynamic both with respect to the source and gap, both of which affect the current waveform. An intuitive mix of these processes, among others, is necessary. In which case, so as to be able to explain and utilise the various measured quantities, the knowledge, then, of the differences between computed and observed parameters and waveforms are indicative of the degree to which gap dynamics have been understood.

The prerequisite is that all the model assumptions made should not complicate the radiative behaviour of the source, to the point of preventing solution of the resulting differential equations in closed, algebraic form. Closed form integrals involving the complex hyperbolic functions allow a single formula regardless of damping conditions in the excitation current simulation.



Fig. 4.4 Conceptual model for a simulative study of the sliding spark discharge source

But there is a fundamental limit as to the complexity of closed form models that can comfortably be solved. A closed form integral makes use of the solution of third order differential equations. Differential equation solutions are available only for comparatively simple functions with few variables, few simultaneous equations, and low order derivatives: except for special cases, the most complicated equation(s) for which a closed form solution of linear differential equations with constant coefficients exists for arbitrary parameter values is a fourth order equation. Algebraic complexity (which limits the precision of any model) creates problems for higher, notwithstanding, even for third order equations.

Further, some quantitatively explicable effects cannot be simulated with closed form models. Modification of the closed form is required however if one has to account, for instance, for dynamic impedance changes. Various approaches and assumptions e.g., Laplace transforms, can be used to solve the resulting equations. Numerical models are also necessary. Numerical approaches allow the simulation of almost any complex model that can be conceived, to be done with closed form modelling of the source. Particularly advantageous is the fact that non-linear numerical equations are nowadays easily solved by use of computer: numerous algorithms are available for increasingly complex solutions. Three relatively common methods are known: series approximations - e.g., the Runge–Kutta, predictor-error, and the extrapolation, procedures [134].

4.3 Sample Matrix Atoms Excitation Processes

New, important applications of ultra-short pulsed atmospheric pressure plasmas have attracted considerable effort in recent years in the study of high rate energy liberation in high voltage breakdown devices especially those in which there arises light flashes and radiation emitting discharge plasmas along the surface of dielectrics. For instance, intense light flashes of duration shorter than 100 ns are conveniently obtained from the different varieties of sparks discharging in air atmospheres.

Ionisation and excitation in these discharge plasmas are governed by similar equilibrium, but ionisation (which requires more energy in any excitation system) proceeds to a lesser extent than does excitation. In the sliding spark this is confirmed from the proportion of the measured neutral lines relative to the ionic lines: the ions that are not totally ionised in the sliding spark (as in any other laboratory plasmas) have a large number of highly excited levels.

The atomic properties of low-density plasmas can be represented by isolated ions in which the entire charge density of the ion is from electrons in bound states (plus the nuclear charge). In a high-density plasma, however, the electronic charge density has a bound state part, as in the isolated ion case, and a free electron density part which can be taken to be constant to a finite radius outward, with sufficient charge to neutralise the ion.

The emission characteristics of the sliding spark discharge plasma are due, first, to the high current densities attained, which allow multiple electron–atom collisions and thus excitation to high energy states of the atoms vaporised from the sample matrix; and second, due to the small concentrations of cathode atoms in the gap, because of the very short duration of the discharge. The source parameters favour the production of very spark-like spectra. The neutral atom beams are dispersed into the expanding plasma and are excited and emit radiation because of their interaction with the ions and electrons in the plasma column.

In addition to the dependence on the rate of change of the maximum current, the ionisation and excitation rates in the sliding spark discharge plasma are also related to the ionisation potentials of the vaporised species and the surrounding air.

The measurements reported in this dissertation suggest that collisional excitation, radiative decay and collisional ionisation are predominant in the formation of the sliding spark discharge plasma, with collisional de-excitation making a small contribution. Electron impact excitation builds up population in the long-lived metastable levels, which are then ionised directly by additional electron collisions. The influence of other processes such as three-body recombination, radiative recombination, autoionization, and dielectric capture is negligible.

4.31 Quantitative Analytical Spectroscopy

The excited species in the sliding spark discharge plasma can be studied and characterised by the analysis of its radiation. Signals obtained by any passive spectroscopy on a plasma contain information about temperature, density and flux of the main plasma species, and are a signature of their identity and concentration. Spectroscopy in the visible, VUV, XUV and soft X-ray regimes can also contain a wealth of information on the atomic (and ionic) processes in the plasma. The plasma emission in these spectral regions consists of continuum radiation (bremsstrahlung and recombination radiation) and line radiation. The intensity of the continuum radiation is a complicated function of the electron temperature and density of the species content. In order to determine the radiant emission from a discharge plasma absolutely it is necessary to first know what atoms and ions are present and their concentrations. The equations for computing the equilibrium composition of plasmas are fairly standard. However, different conceptual approaches are used in computing the partition functions. A typical laboratory plasma may not be fully ionised but it possesses a high number of highly excited levels; in order that it be tractable thus, it is necessary that some approximate mathematical treatment of the atomic processes, e.g., distorted wave approximation [135] involving such levels be used to modify the ionisation cross sections on rates to include the effect of the lowering of the continuum, or the effect of excitation to highly excited levels that do not merge with the continuum.

Based on the measured spectroscopic temperature and electron densities data reported in the literature and computed in this dissertation, the origin of radiative emission from surface discharge plasmas can be ascribed to three mechanisms: Electron–ion free-free transitions (bremsstrahlung continuum), overlapping free-bound transitions, and bound-bound transitions (atomic and ionic line spectra). Other possible mechanisms such as electron-neutral or attachment continua, can be neglected. For the electron temperatures estimated for a typical sliding spark discharge in this dissertation and elsewhere [26], it can be considered that a significant fraction of the total emission is due to recombination continua for wavelength < 400 nm. In the UV region where the plasma tends to be optically thin, a large fraction of the radiation is due to highly broadened and intense line emission.

The quantitative interpretation of the measured line intensities demands the knowledge of atomic physics describing specific radiation from plasma. The cross sections for collisions of atoms with electrons and ions and the oscillator strengths for radiation processes must be known or be calculated to considerable accuracy. Ordinarily, calculations for radiative plasmas are based on energy levels and dipole transition rates of isolated atoms and ions. But when the density of the plasma is high enough, the energy levels of bound electrons are shifted by the Coulomb interactions with the free electrons, and some account for this phenomenon must be taken into
consideration. Some levels can even be pushed into the continuum (pressure ionisation). When this occurs there is transfer of oscillator strength from line to continuum absorption [136].

The starting point for the calculation of the energy of an excited electron in a one-electron system is the solution of the Schröndiger equation in the central field approximation of a nucleus charge Z. One ends up with eigenvalues E_n expressed as a function of only the principal quantum number, n, thus,

$$E_n = \frac{R_y Z^2}{n^2}$$
(4.13)

where R_{y} is the Rydberg constant.



Fig. 4.5 Schematic representation of a molecular energy level diagram

In a many-electron-system the field for the outer electron may be considered central still but no longer Coulombic; so, n has to be replaced by the effective quantum number n_{eff} . If d_c is the

correction for the quantum effect, $n_{eff} = n - d_c$. In the case of diatomic molecules, a typical example of whose level diagram is shown in Fig. 4.5, other energies contribute to Eqn. 4.13.

Apart from the energy levels corresponding to different electronic arrangements, there are also different states, which account for the vibrational and rotational modes. In the case of polyatomic molecules, stretching and bending modes can also occur in addition; these are not necessarily disadvantageous in analytical spectroscopy since they can help in qualitative analysis. In order to easily mathematically account for the additional vibration and rotation energy, the classical case of an harmonic oscillator oscillating with a frequency v_H and rigid rotation (*Rot*), is considered; this leads to the relation

$$E_{v_{H},Rot} = \left(n_{v} + \frac{1}{2}\right)hv_{H} + \Omega_{Rot}(n_{Rot} + 1)$$
(4.14)

where Ω is the [effective] rotational constant, and n_v and n_{Rot} are the respective vibrational and rotational quantum numbers.

4.32 Spectral Line Emission Characteristics

In the case of a plasma-source quantitative spectroanalysis scheme based on the sliding spark discharge three main emission mechanism need to be considered: bound-bound (*or line, l*), free-bound (*f-b*), and free-free (*f-f*) transitions. When considering free-free continuum with respect to sliding spark there are in turn two cases to focus upon. First, there is the free-free transitions involving electrons and ions, and second, the free-free transitions involving electrons and the neutrals. However, the electron-neutrals free-free continuum is unimportant except at low electron temperature excitations such as in the cooler peripheries of the fully expanded plasma column.

For precise quantitative work, the spectral free-free contributions from each species need to be added together to obtain the total free-free contribution. The spectral wavelength (λ)-dependent emission coefficient \in_{λ} is thus the sum of the emission coefficients for each mechanism:

$$\epsilon_{\lambda} = \epsilon_{i,\lambda} + \epsilon_{f-b,\lambda} + \epsilon_{f-f,\lambda} \tag{4.15}$$

 $\in_{\iota,\lambda}$ can in turn be obtained by adding together the spectral emission coefficients of individual measured lines that affect the wavelength of interest. The wavelength-dependent emission coefficients of each individual line can be implicitly derived from the integral intensity relation (Eqn. 4.20) taking into account level occupation probabilities [137].

For spectroscopic as well as engineering work, wavelength quantities (integrated emission coefficients and the net emission coefficients) are more desirable than spectral values. In optically thin plasmas, the intensity of line radiation is determined by the wavelength's emission coefficients. The wavelength integrated emission coefficient \in is given by

$$\in = \int_0^\infty \in_\lambda d\lambda \tag{4.16}$$

Eqn. 4.16 is an expression for the total radiant power emitted by a plasma per unit volume per unit solid angle in the absence of absorption. The zero length net emission coefficient is equivalent to the wavelength-integrated emission coefficient (Eqn. 4.16). The net emission coefficient is defined as the derivative of the intensity, I, evaluated at the end of a line-of-sight path length l into an isothermal, homogeneous plasma. It can be expressed in the form

$$\mathbf{I} = \int_{0}^{\infty} b_{\lambda} \left\{ 1 - \exp\left[-k'(\lambda)l\right] \right\} d\lambda$$
(4.17)

where b_{λ} is the Plank's blackbody function, and $k'(\lambda)$ is the spectral absorption coefficient including induced emission. Surface discharges do not radiate as ideal black bodies and the assignment of a brightness temperature requires a wavelength specification.

In the quantitative spectroscopic application there should be a restriction to the optically thin atomic transitions arising from [presumably] homogenous, isothermally emitting zones in the discharge plasma.

Between an upper energy level E_i and a lower level E_j of an excited atom in a system there are three types of possible radiative transitions: spontaneous, stimulated emission and absorption all which occur with a frequency V_{ij} given by the well-known Eqn. 4.18, from which the unperturbed centre-line emission wavelength can be directly deduced thus

$$hv_{ij} = E_i - E_j \tag{4.18}$$

Spontaneous emission is characterised by a transition probability per unit time, A_{ij} . The other two (stimulated emission and absorption) are dependent on the presence of a radiation field, so they are more important in the interaction of e.g., a laser field with atoms. Dipole transitions have the largest values and are, therefore called 'allowed'; the lifetime of the excited state E_i , its transition probability into lower states *j*, and the absorption oscillator strength are related.

For a given atom Eqn. 4.18 gives rise to a single line or well separated bunch of lines (multiplets). In the case of molecules, Eqn. 4.14 gives rise to bands. Transitions between the

rotational levels lead to equidistant lines mostly in the far infra red (~100 μ m), where as those between vibrational levels result in lines in the near-IR (~ 1 μ m). The spectrum can be written as [138]

$$\Delta E = h\nu_H + 2B(n_{Rot} + 1)[-2Bn_{Rot}]$$
(4.19)

with a so-called 'R-branch' and [] with a 'P-branch' for all $n_{Rot} = 0$, (1,2,...). In transitions between different electronic configurations much higher energies (~ eV) are involved (visible, and UV region) and can also lead to bands, the intensities and observed vibrational structure of which are explained by the "Frank–Condon" principle [139]. Although the $\Delta n_{Rot} = 0$ transition is forbidden in a pure no-vibrational case, this can occur in the latter case giving rise to an additional 'Q-branch'.

The integral line intensity I_{ij} from a given spectral transition is computed from the relation

$$I_{ij} = N_i A_{ij} h v_{ij} = \left(\frac{N_i h v_{ij} A_{ij}}{4\pi}\right) \times 10^{-7} \text{ Wcm}^{-3} \text{ sr}^{-1}$$
(4.20)

where N_i is the number density of state *i* (cm⁻³), *h* is Planck's constant, *v* is the frequency of the transition (s⁻¹) and A_{ij} is the Einstein spontaneous emission transition probability into the lower level (s⁻¹). Transition probability by unit time - $N_i A_{ij}$ - is the number of photons emitted per unit time. Although not significant in spectrochemical analysis sources, when the radiation flux is high, Eqn. 4.18 should be modified to take into account induced transitions.

Assuming the radiating discharge plasma column is in thermal equilibrium, the number of species in the ground state, N_0 , is related to the total number of atoms present, N_T , in the plasma by

$$N_o = N_T (g_o / \mu) \tag{4.21}$$

where μ is the partition function (normally, $\mu = \sum_{n} g_n \exp(-E_n / \kappa T)$) and g_o is the statistical weight representing the number of degenerate levels in the ground state. The values of v, g, A_{ij} , E_{ij} can be obtained from Corliss and Bozman tables [140]. Temperature dependent functions can be computed from the polynomial functions published by de Galan *et al.* [141]. When the temperature of the source is low, or when the lowest excited state is relatively high in energy, only the first terms in the series for computing the partition function, with E = 0, is important, so $\mu \approx g_o$ so that the number of species in the ground state, N_0 , is approximately the same as the total number of atoms present in the system, N_T . In practical cases, however, there will be a small fraction of the atoms in excited states. The number of species in an excited state, N_i , and the number of species in the ground state, N_o , can thus be related by the well-known Boltzmann equation,

$$N_i = N_a (g_i / g_a) \exp(-E_i / \kappa T)$$
(4.22)

where the ratio g_i/g_o corresponds to the statistical weight representing the number of degenerate levels in each state and *T* is the temperature (K). E_i is the excitation energy of the transition, and κ is the Boltzmann constant. If j_m is the orbital angular momentum quantum number of the energy levels *m*, the states, g_m , are explicitly given as $g_m = 2j_m + 1$.

Combing Eqn. 4.19 and Eqn. 4.20 gives the [complete] Boltzmann equation

$$N_i = N_T (g_i / \mu) \exp(-E_i / \kappa T)$$
(4.23)

which approximately describes a plasma under local thermal equilibrium (LTE), i.e., where the collisional population and depopulation processes of the electronic energy levels in the excited atoms are in equilibrium with their reverse processes. If the electron–ion-recombination coefficient is sufficiently larger than the recombination time, then the ionisation of the plasma will remain in equilibrium with its temperature since, under these conditions the ion density is a sensitive function of the plasma temperature. This relation is, however, only applicable for electron densities, n_e , beyond a certain threshold given by [142]

$$n_{e} \geq 7 \times 10^{18} \left(Z^{7} / n^{17/2} \right) \left(\kappa T / Z^{2} \chi_{H} \right)^{\frac{1}{2}} cm^{-3}$$
(4.24)

where χ_H is the ionisation energy of hydrogen. The use of the above relation [also] presupposes that a single temperature can be used to describe the population distribution of excited states for the analyte species; in the case of the sliding spark, this is not exactly true.

The energy of the transition is hv_{ij} . Integration over the line of sight *dl* results in the measured line intensity thus

$$I = \int \frac{h\nu_{ij}}{4\pi} N_i A_{ij} dl \tag{4.25}$$

A difficult problem that is frequently encountered in plasma measurements, is the deduction of local values of the quantity under study from integrated values of the quantity measured along a chord through the plasma. In a typical cylindrical plasma such as the sliding spark discharge, the projection of the detectable emissivity along straight lines should be measured as a function of position along a line perpendicular to the line of sight; from this data the emissivity must be

reconstructed. In practice, the temperature in the plasma column, and therefore the spectral emission coefficient, differs from atom to atom, and from region to region in the discharge. Reconstruction of a cylindrically symmetric function from its projection can be made by several methods. The most common type of the integral equation used nowadays is that which was first proposed by Abel in the 19th century, since which time, due to its wide relevance in science and engineering a plethora of related reconstruction techniques have been proposed in the form of the Abel transform.



Fig. 4.6 An example of the sodium atomic energy levels in the Grotrian diagram²

There are many approaches for practically solving the Abel's integral equation: Graphical methods [143, 144]; variable transform techniques [145,146]; iterative techniques [147,149]; curve fitting methods [150,151], and integral transform techniques [152,153]. The Abel inversion process gives the relationship between the radial profile of the emissivity $\in_{\lambda} (y)$ and the measured intensity on each chord $I_{\lambda}(y)$. Since spectrochemical sources usually have an axial geometry, with a variation along the length of the discharge, the Abel inversion may be used to relate the intensities measured along the projected image of the discharge and the intensity

 $^{^2}$ Each energy state is designated by —. The angled lines indicate possible transitions. The line darkness indicates the relative transition intensity. The number on the line is the wavelength in angstroms of the emitted (or absorbed) radiation

emitted by small volumes within the discharge, which are a function of the radial distance from the centre of the discharge annulus, the only difficulty in the method being the requirement that the source have temporal and spatial stability during measurement; that is a reasonable assumption in the sliding spark.

For a cylindrically symmetric, optically thin, extended radiation source, the relationship between the emissivity $\in_{\lambda} (y)$ and the measured intensity, $I_{\lambda}(y)$, as detected from outside the source is given by [154]

$$I_{\lambda}(y) = \int_{-\sqrt{a_r^2 + y^2}}^{+\sqrt{a_r^2 + y^2}} \epsilon_{\lambda}(r) dx$$
(4.26)

for a particular wavelength λ , where y is the displacement of the intensity profile from the plasma centreline, r is the radial distance from the centre of the source $(x^2+y^2 = r^2)$, and a_r is the source radius. It is assumed that $\in_{\lambda} (y)$ vanishes for r > a, hence $I_{\lambda}(y)$ vanishes for $/y / > a_r$. For simplicity, it may be taken that $a_r = I$; supposing a scale factor, and changing the variable of integration to r, Eqn. 4.26 may be written in the form



Fig. 4.7 Illustration of co-ordinate system and geometry of an extended radiation source³

³ Cylindrically symmetric with respect to the Z-axis, which is normal to the paper.

Applying the Abel transform, the radial distribution of the plasma emissivity from the line of sight can be written as

$$\epsilon_{\lambda}(y) = -\frac{1}{\pi} \int_{r}^{l} \frac{dI_{\lambda}(y)}{dy} \frac{dy}{\sqrt{y^{2} - r^{2}}}$$

$$(4.28)$$

This function should vanish beyond the finite plasma radius.

For plasmas that do not meet the optically thin criteria another form of the equation must be used. The inclusion of non-parallel rays can be handled as well, perhaps using methods similar to those used in computerised tomography [155].

4.33 Measured Spectral Line Profiles

Eqn. 4.20 may be combined with Eqn. 4.23 to give

$$I_{ij} = N_T (g / \mu) A_{ij} h v_{ij} \exp(-E_i / \kappa T)$$

$$(4.29)$$

which expresses the total intensity of a spectral line radiated in all directions by a radiative plasma. When measurement of this intensity is made along a particular direction, corrections must be made for the geometry and efficiency of the optical system and for the response of the detector employed.

In the above equation A_{ji} may be replaced by terms reflecting explicit atomic constants. In that case the properties of specific elements (atoms) under study are invoked, which is more practical in quantitative spectroscopy where a derivation based on the classical model of radiation emission by an oscillating charged particle can easily be made. This approach is also advantageous for the simultaneous consideration of absorption and emission intensities, since the product of the oscillator strength with the degeneracy has the same numerical value under both cases i.e., $g_j f_{ij} = -g_i f_{ji}$. The following equation is obtained

$$I_{ij} = N_T (g/\mu) (8\pi^2 e^2 h/m_e c^2) f_{ij} v_{ij}^3 (-E_i/\kappa T)$$
(4.30)

where e, m_e , are the charge and mass of the electron, respectively.

The derivation of Eqn. 4.30 assumes that the intensity is integrated over the total width of the line, and that it is not affected by line absorption. In spectrochemical analysis, the true line width is usually much less than the resolution limit of the spectrometer. In this case the measured peak intensity is proportional to the total intensity integrated over the line.

First, the spectral lines have a natural width due to the finite radiative lifetimes of the emitting atom or ion existing in the upper and lower energy levels of the line (e.g., for deuterium n = 3 level the radiative lifetime is 10^{-8} s). Where as the natural width is usually of negligible importance in radiation calculations, those lines that have autoionization levels can have natural widths larger than the Van der Waals widths, and even as big as Stark widths. However, most species in a typical sliding spark discharge plasma obtained using a source such as the one used in the work reported in this dissertation are not expected to exhibit autoionization levels except at extremely high temperatures, which are not attained. Thus, the natural line widths for lines emitted in the sliding spark discharge plasma can practically be neglected. Much more important is the thermal movement of the particles during the plasma column expansion caused by the initial implosion and expanding shock wave, since this leads to a Doppler shift of the emitted lines. Averaged over a Maxwellian ion velocity distribution the resulting Guassian line shape, which can [also] serve for ion temperature determination, has a half width $\Delta \lambda_{FWHM}$ given by

$$\Delta \lambda_{FWHM} = 2.355 \sqrt{\frac{\kappa T}{Mc^2}} \lambda_o \tag{4.31}$$

where M is the molecular weight of the excited species.

Although accurate line widths are necessary for obtaining correct values of the spectral emission coefficients, the line widths and profiles do not affect the wavelength integrated emission coefficients. As long as all lines selected for the spectrochemical analysis are optically thin, none of the wavelengths-integrated values are affected by the line half widths. It is not until absorption becomes important that the line widths also become significant.

Nonetheless, optical systems, acting as low pass filters, can degrade high frequency information contained in spectra. This leads to line shape distortions, and to decreased line parameter accuracy and poor spectrometer resolving power. In a paper published in 1980 Skupsky [156] has shown, also, that the spectral lines of ions in plasmas are shifted relative to their positions in isolated ions, due to the presence of free electrons in and around the ion. This shift depends on the free-electron density [157]. In the case that a time invariant linear sliding spark spectroscopy system is required, a convolution has to be made as the product of the observed spectrum by the line impulse response of the spectral device [158], in order to recover spectral line parameters such as full width at half maximum (FWHM) and peak position in their natural state before instrumental distortion.

Independently, spectral line broadening is a wide field, which has received much attention in the previous years. The velocities of heavy particles in a plasma, for instance, may be determined by measuring the Doppler shifts of the spectral emission lines.

There is an empirical relation between line profiles, radiative transfer and the atomic populations, which characterise the microscopic state of the plasma. The practically expected profile for the line radiation, emitted from a sliding spark discharge plasma, is the Voigt. The half width of the Voigt w_V , can be approximately expressed in terms of the Lorenz, w_L , and Gaussian, w_G , half-widths by the following expression:

$$w_V \approx \frac{w_L}{2} + \sqrt{\frac{w_L^2}{4} + w_G^2}$$
 (4.32)

The Lorenzian (L) portion of the width in itself consists of four contributions: natural broadening (nb), Van der Waals (vw) broadening, resonance broadening (rb), and quadratic Stark broadening (st) thus

$$w_L = w_{nb} + w_{vw} + w_{rb} + w_{st}.$$
(4.33)

Van der Waals broadening - which is very difficult to calculate for non-hydrogenic atoms - is caused by the interaction between the neutral particles in the plasma. There can also be a Van der Waals component involving ions, but this is always insignificant in comparison to the Stark contribution from the same. Lines with high upper energy levels of complex atoms and ions, though usually weak, may also give rise to the linear Stark broadening. The Van der Waals interaction is more important at lower temperatures, where the Stark contribution is small due to lack of enough charged particles in the plasma. The electron quadratic Stark broadening is the most important broadening mechanism in most thermal plasmas. Although both electrons and ions are responsible for the quadratic broadening, the electron component is dominant.

Resonance broadening occurs due to an atom or ion in a resonance state interfering with another like atom or ion in a ground state - an interaction in which there may occur a transfer of energy from the excited atom or ion in the ground state.

External electric fields (> 1 kV/cm), which are rarely reached in a non-magnetically confined plasma device, can give rise to level splitting due to the Stark effect. This can result in complicated line broadening depending on the types of excitation mechanisms involved [138].

On the other hand there are many lines that are detected in sliding spark spectroscopy which possess self-reversals with deep troughs in the centre, which testifies to the presence of an

extended absorption atomic layer surrounding the hot discharge central column. Line reversal is a pronounced phenomenon in dense inhomogeneous plasma having a considerable ionisation, where Stark spectral line broadening by electrons and ions is predominant. The asymmetry of the quadratic Stark effect is usually radiated by low temperature plasmas. The asymmetry of the selfreversed line wings influenced by the linear Stark effect is related to the Doppler effect.

Asymmetric self-reversal in dense plasmas is mainly due to the variation of local broadening profile P(v,r) in the radial (*r*) direction, and may be interpreted quantitatively by introducing different average along-the-line-of-sight shifts of broadened emission and absorption profiles. Theoretically, symmetric self-reversal normally applies to the case when the broadening profile does not depend on the location in the plasma, i.e., P(v,r) = P(v). P(v,r) is the profile normalised to unit area over a frequency range describing the broadened line shape in emission and absorption (thin layer profile).

Simplified approaches for computing the line shapes of spectra emanating from complex plasma discharges are best associated with emission and absorption model theories, or by parametric approximations of their variations in the radial direction, proceeding from the most general ideas. Atomic transitions involving self-reversed spectral lines due to the Stark effect exhibit a broad absorption line when irradiated by an intense continuum source. The profile P(v,r) of spectral lines influenced by the quadratic Stark effect may be assumed [159,160], with allowance for the fact that in the homogeneous plasma, the half width, shift and other parameters associated with the layer profile vary from point to point.

The thin layer profile, to a first approximation, is close to the Lorenzian,

$$P(\nu, r) = \Delta \lambda_{FWHM} / \left\{ \pi \left[\left(\nu - \nu_o - \Delta(r) \right)^2 + \left(\Delta \lambda_{FWHM} \right)^2 \right] \right\}$$
(4.34)

where $\Delta(r)$ is the shift in the maximum profile P(v,r) relative to the unperturbed central frequency v_o . For the spectrochemical utility of the sliding spark discharge only optically thin emitting spectral lines are considered. In this way, one is able to assume a line width profile that is predominantly caused by the Doppler effect (in the general case of non-Maxwellian distribution the line shape is not Gaussian); the velocity distribution of the species, $\rho(v)$, is related to normalised distribution of the emitted radiation q(v) in a specified direction by the equation

$$q(v)dv = \rho(v)dv, v = \frac{c}{v_o} \left(v - v_o \right)$$
(4.35)

where v, v_o are the Doppler-shifted and unshifted frequencies respectively, and c is the speed of light.

The normalised spectral line profile is related to the line intensity I(v) by [161]

$$q(v)dv = \frac{I(v)dv}{\int_{-\infty}^{\infty} I(v)dv}$$
(4.36)

Multiplying $\rho(v)dv$ by v, integrating over v, and using the above equations the equation for the determination of the mean particle velocity along beam of observation (so-called the beam velocity of the species in the discharge plasma), is obtained

$$\upsilon = \int_{-\infty}^{+\infty} \rho(\upsilon)\upsilon d\upsilon = \int_{-\infty}^{+\infty} q(\upsilon) \frac{c}{v_o} (\upsilon - v_o) d\upsilon = \frac{c}{v_o} \frac{\int_{-\infty}^{\infty} I(\upsilon) (\upsilon - v_o) d\upsilon}{\int_{0}^{\infty} I(\upsilon) d\upsilon}$$
(4.37)

which is related to the plasma temperature and its distribution in the discharge.

4.4 Plasma Temperature and Electron Density

Among the important parameters characterising a discharge plasma and its relationship to spectroscopic analytical performance, is the electron temperature. The electron temperature (T_{e} -) is the central parameter, the knowledge of which is also fundamental with a view to developing any plasma technological applications. Knowledge of the temperature and electron density is vital to understanding atomisation, ionisation and excitation in the discharge plasma. With respect to quantitative spectroanalysis using the sliding spark two factors influence the species' emitted line intensity: the number density of the atoms, and the temperature of the plasma. The number density of free atoms is dependent on the mass of sample ablated and on the fraction of material vaporised in the plasma. The vaporised amount depends on the plasma shielding and on the absorption of the liberated energy, which is in turn related to the density of the element in the plasma.

The kinetic temperature of the electrons is usually associated with the excitation temperature (T_{ex}) since excitation processes are mostly caused by electrons. This statement is even truer if the plasma has high electron density (e.g., an atmospheric pressure plasma). As a result, the methods for the determination of T_{e-} at atmospheric pressure are frequently based on calculation of T_{ex} . When the plasma is in LTE, it is characterised by a single electron temperature. Thus, the interpretation of the plasma is unambiguous and can be considered as equal to the electron

temperature. LTE is reached when the electron density of the plasma is high enough to ensure that the electrons are solely responsible for the mechanisms of excitation/de-excitation in the plasma. In particular the distribution of the excited levels follows a Maxwell-Boltzmann distribution with an excitation temperature T_{ex} being equal to the electron temperature T_{e-} . LTE is best well admitted for low pressure plasmas; it is achieved when the electron density is higher than a critical value, n_c , which, for hydrogen-like ions, is given by [162]

$$n_c = 1.5 \times 10^{18} Z^2 (T_e / Z^7 10^6)^{0.55 - (0.49/Z)^{\frac{1}{2}}}$$
(4.38)

where Z is the nuclear charge.

Optically thin plasmas permit direct measurements of plasma density and temperatures that are independent of line spectral data because they minimise line profile errors attributable to optical thickness. The density and temperature of optically thin plasma may also be measured independent of spectral measurements using interferometry, absorption and absolute emission plasma diagnostics. When precise knowledge is obtained about the electron temperature and density from the various available plasma diagnostics, the impurity enhancement factor (related to the effective charge (Z_{eff}) of the plasma) may be obtained from measurements in the line-free spectral regions. Measurements of line intensities, broadening and shifts combined with modelling, can also yield valuable information on ion densities, temperature and plasma rotation. For many of these measurements, a good spectral resolution is of importance. Indeed to be able to understand the detailed plasma processes it is desirable to measure the various parameters with as good spatial and temporal resolution as is possible. The temporal resolution is on one hand dictated by the statistical properties of the process under consideration (e.g., the minimum amount of time needed to collect enough photon spectra, etc.), and on the other hand by instrumental properties (e.g., the read-out time of a CCD detector or the repetition rate of pulsed discharge circuit). Spatial resolution is in most cases dictated by the geometry of the measurement set up and not so much by the physical process under study. Passive spectroscopy are essentially line-averaged. The spatial resolution in a direction perpendicular to the viewing direction depends on the detector etendue.

In principle T_{e} can be measured using both equilibrium and non-equilibrium Boltzmann excitation statistics [163-165], absolute continuum line intensity [166,167], continuum-to-line emission intensity ratios [164,168], emission line reversal [167], Doppler broadening [167,169], Langmiur probes [170] and Thomson scattering techniques [171, 172]. Techniques for characterising the plasma electron density include equilibrium Saha statistics [173], Stark broadening [167-174], interferometric plasma refractive index measurements [167,175,176], and Langmiur probes [170]. At atmospheric pressure, Thomson scattering (very appropriate for high

electron densities > 10^{16} cm⁻³ or higher) cannot used due to its weak cross section for scattering [177]; it is also difficult to implement in electron densities in the order of 10^{14} cm⁻³.

In optical breakdown on the other hand plasmas in nominal high pressure gases, studies of H₂ and hydrogenous molecules can also take advantage of the comparatively large Stark-broadening of the H-atom spectra to determine n_e (Stark-broadened H_{α} emission lines) [178-183]. Electron temperature can then be inferred from the Boltzmann plots of the hydrogenic Balmer series.

Although the standard method to measure n_e of a dense plasma is based on the Stark broadening of spectral lines [159], in the case where the peak electron densities reach as high as 10^{20} cm⁻³, the applicability of Stark broadening method is not viable - because of the strong line broadening and high background intensity caused by the bremsstrahlung and recombination effects [184]; Stark broadening of spectral lines depends weakly on the plasma temperature.

It may happen that the excitation/de-excitation scheme of the excited atom populations is uniquely governed by the reverse reaction

$$A_i + e^- \leftrightarrow A_j + e^- \tag{4.39}$$

In this case, the electron energy distribution function (EEDF) is Maxwellian, and the populations of the levels are related through the Boltzmann relation (so $T_{e-} = T_{ex}$).

When production and loss of the ions is exclusively controlled by the reaction

$$A_i + e^- \leftrightarrow A^+ + e^- + e^-, \tag{4.40}$$

it is found that the population of the level *i* is linked to the ion density n^+ by the Saha formula.

When the Saha equation is obeyed only by a few levels, these levels are said to be in partial local Saha equilibrium (pLSE), which is interrelated to the Boltzmann relation. Complete LSE requires that electron–impact ionisation be balanced by three-body recombination according to reaction

$$(A_i + e^- \leftrightarrow A^+ + e^- + e^-) \tag{4.41}$$

Contributions are possible from other loss mechanisms (like diffusion or dissociative recombination). That means that in the charged particles balance, the creation term (ionisation) is larger than required by the Saha conditions, so, because enhancement of electron-impact ionisation is accompanied by enhancement of electron-impact excitation, the excited levels are

overpopulated with respect to the Saha equilibrium (the ionising plasma). The reverse case is also possible (recombining plasma). In both plasmas, when approaching the continuum limit, a state of equilibrium is reached in which those excited levels sufficiently close to the continuum (ionisation) limit come in equilibrium with the electron temperature. The corresponding excited states can thus be used to determine T_{e} .

Thus, special care must be excised in choosing levels to compute the electron temperature. Two different situations are possible in this respect: in an ionising plasma, a spurious excitation temperature can be obtained, which is lower than the actual one; on the contrary, in a recombining plasma, a higher spurious temperature can be found. The second approach is mostly obtained based on absolute emission intensity measurements of a line from which the absolute population of the upper level corresponding to the transition is calculated.

It is possible to modify Eqn. 4.29 and Eqn. 4.30 to account for self-absorption; the equations become considerably complex, however, in which case it is preferable to consider only lines, which show little or no self-absorption, i.e., when the source is optically thin. In that case, the equations imply, even for a homogenous source, absolute temperature measurement may be made only if the line intensity (i.e., the total line emissivity, integrated over the whole line profile) can be measured on the basis of the total number of atoms present in the system.

It is simpler to determine the temperature from the relative intensities of two lines from the same emitting species but with different excitation energies .

If the substitutions $\lambda = c/\nu$ (where λ is the wavelength of the emission in vacuum) and $I_1 = I_{ij}$, $I_2 = I_{nm}$ are made, manipulation of Eqn. 4.29 yields

$$\frac{I_1}{I_2} = (g_1 A_1 \lambda_2 / g_2 A_2 \lambda_1) \exp[(\Delta E) / \kappa T]$$
(4.42)

where $\Delta E = E_2 - E_1$, or in its classical form (obtainable from Eqn. 4.30)

$$\frac{I_1}{I_2} = (g_1 f_1 \lambda_2^3 / g_2 f_2 \lambda_1^3) \exp[\Delta E) / \kappa T]$$
(4.43)

both of which equations enable the determination of the temperature of the spark discharge plasma without knowing the number of atoms of the emitting species which are present or the response of the optical system (including the CCD detector used).

However, if the two lines whose intensity is measured are not close in wavelengths, it is necessary to determine the [relative] response of the system separately at the two wavelengths by means of a standard emission source. Also, the values of A and f reported in the literature have large uncertainties, being better known and reliable for longer, than the shorter wavelengths, and for lighter elements than the heavier ones – they can be a source of random errors in the intensity measurements. Further inferences may be made based on Eqn. 4.43. By differentiating Eqn. 4.43 one readily obtains

$$\frac{\Delta T}{T} = \frac{\kappa T}{\Delta E} \cdot \frac{\Delta R}{R} \tag{4.44}$$

where $R = \frac{I_1}{I_2}$. Eqn. 4.44 shows that if $\frac{\kappa T}{\Delta E}$ becomes comparable or larger than 1, the errors in the relative line intensities are magnified.

The accuracy of determining the plasma temperature based on the relative spectral line intensities may be improved by observing several lines and by plotting properly the level populations verses the energy of the upper level (the so-called Boltzmann plot).

Re-writing Eqn. 4.29 and Eqn. 4.30 in logarithmic form, and re-arranging the terms,

$$\log\left(I_{ij}\lambda_{ij} / g_i A_{ij}\right) = \log k - 0.4343E_i / \kappa T \tag{4.45}$$

and

$$\log(I_{ij}\lambda_{ij}^{3} / g_i f_{ij}) = \log k' - 0.4343E_i / \kappa T$$
(4.46)

where the factors k and k' include those constants from Eqn. 4.29 and Eqn. 4.30 which are not explicitly included, and $0.4343 = log_{10} e$. When a plot is made of the LHS of Eqn. 4.45 (or Eqn. 4.46) vs. E_i for a number of emission wavelengths, the points should in principle fall along a straight least squares fitted line with a slope equal to $-0.4343/\kappa T$ (where κT is the thermal energy), from which the plasma temperature is readily found. (Theoretically, any curvature of the line would be an indication of departure from thermal equilibrium).

The beauty of the Boltzmann plot method is that only relative line intensities have to be measured, which is easier than absolute measurements of the same quantities. Also, the computed temperature based on this method does not depend on the plasma parameters. But the accuracy of the results is usually poor at high temperatures because the ratio of the line intensities is fairly insensitive to the temperature at such temperatures.

Fig. 4.8 (a & b) show a plot of Eqn. 4.46 from the sliding spark intensity data of some of the successfully excited, detected and measured lines. It is clear that the sliding spark discharge exhibits neither the Boltzmann thermal equilibrium exactly nor is it homogenous. Departures from equilibrium are implied in the scatter of the lines around the regression line, which is fitted with the help of standard linear regression methods utilising mostly those lines which showed little or no self-absorption (i.e., optically thin lines) that were also selected for quantitative analysis. The use of such regression lines indicated in Fig. 4.8 as a benchmark for all the lines detected and measured is important to verify whether the sliding spark plasma is not optically thick to the lines selected and used for quantitative analysis.

The determination of the electron temperature is also possible using relative intensities of spectral lines from the same element but from successive ionisation stages. This would suffice to overcome the sources of error due to the small differences in the upper energy levels of the spectral lines in the Boltzmann plot method – the energy difference is usually increased by the ionisation energy of the lower in ionisation stage. (In the Boltzmann plot method the main source of inaccuracy is the small difference in energy of the upper levels of spectral lines from the same ionisation stage). However, the use of lines from ionisation stages, which are even further apart, is hindered by the fact that the condition for LTE for the upper levels of such lines will not be met in practice.

The ratio of the relative intensities for lines from successive ions is also given by much more complicated mathematical formulae that must include the (plasma) Debye length and ionisation energy of the H atom, the Bohr radius, and the electron density. Plasma corrections of the energy must also be made. In principle, in order to derive the temperature, one must know the electron density; in addition, to calculate the energy difference, one must know both temperature and electron density. In practice this ambiguity may be solved by assuming an initial temperature and calculating the entire procedure repeatedly using iterations.

In this work the Boltzmann plot method was used. The temperature was estimated to *ca* 7750 K using the Fe I data. While using O II data the same method gave a temperature of *ca* 16100 K, which compares well with the temperature values obtained for the same O II data based on the relative intensities computation: 16500 K. The temperature values obtained are consistent with earlier ones reported by Golloch and Seidel [26]: *ca* 7000 K when using the neutral lines, but higher than the 14000 K they obtained when using the singly ionised lines of Ti and Ca respectively computed based on the relative intensities method. However, the Boltzmann plot method with Ti I data in this work yielded T \approx 3500 K, which is appreciably lower than the presumed average value obtained based on the above estimates in both works. The value from Fe I is higher than that normally obtained for the same from plasma jet sources (5000 K).



Fig. 4.8 Computation of the sliding spark plasma temperature by the Boltzmann plot method

It can be concluded that indeed the temperature in an air-borne plasma at atmospheric pressure is generally low, typically lower than 8000 K [125] only when averaged over the variations in the different parts of the discharge, being highest at the core of the plasma column where there is maximum ionisation, and lower outside. The following arguments, based on the gasdynamic and radiative nature of the sliding spark discharge may explain the phenomenon.

Due to the high particle density, the energy in the sliding spark discharge is distributed through a very large number of excited levels (atomic levels but also through the set of vibrational levels of electronic configurations of the molecular species excited in the binder matrix and in the surrounding air molecules). Further, the energy transfer by elastic electron–heavy particle collisions, is also relatively inefficient. And lastly, peaks exist in the variations of the thermal conductivity in the plasma, corresponding to the physical-chemical reactions between the various components that constitute the plasma; these peaks strongly favour energy losses by heat conduction in the sample substrate surface layers.

There are other possible explanations not only for the temperatures attained in the discharge but also valid for the temperature differences (or distribution in the plasma discharge) too.

The accuracy of the computations is based on selecting lines carefully from a large database; the lines chosen should have a large range of upper energies levels as possible to strictly ensure this. In this case it was not possible since we relied on those few measured lines detected within the present spectrometer band width, excitation capability and interference from the air bands and lines. The chosen lines must be well-resolved for accurately determining the intensities.

There are many lines, especially from neutrals which are detected in sliding spark spectroscopy but which possess self-reversals with deep troughs in the centre, or short dynamic ranges due to self-absorption as compared to ionic lines, which testifies to the presence of an extended absorption atomic layer surrounding the hot discharge central column. The line transitions from the substrate species within the high temperature plasma channel are thus absorbed by the cooler vaporised particles travelling with the shock wave front. The centre of the discharge is normally at a higher temperature than the outer regions; there may also be hotter areas nearer the electrodes. Furthermore, the properties of the spark discharge change very rapidly with time during each discharge. The particle density distribution in the excess of 4000 K. Lower temperature estimates will thus be obtained as is the case with the Ti I lines (3500 K) for the light neutral species which are more likely to be most displaced radially outwards from the core of the plasma column with the expanding shock wave, hence the difference in the temperature estimates between the Fe I and the Ti I.

More accurate values may only be obtained with neutral lines especially when more research is done to use time gating to separate neutral lines from the continuum. Time–resolved emission spectroscopy should also be able to give a clearer picture of the discharge development with nanosecond temporal resolution. Astin *et al.* [185] studied a copper plasma in air at atmospheric pressure and found that self-absorption and line broadening can be reduced using time-delay. Consequently, most researchers use time-gating to separate atomic lines from the continuum.

The initial plasma contains exclusively multiply charged ions. When the ablation current is terminated, electrons decelerate and a massive continuum emission is produced. The continuum is due to bremsstrahlung emission and ion-electron recombination. When the spark current ceases, the plasma ion density and temperature begin to decay. The differences in the decay time (Eqn. 4.12) between the ionic and atomic lines provides a further mechanistic insight into the computed temperature values and their distribution. A few hundred nanoseconds later, ion and atomic line emission dominate the spectrum. Atomic (neutrals) vapour in the post-discharge region, for instance, has a lifetime of about 300 μ s following the ceasation of the excitation current pulse. As the plasma expands, it cools and so do the analytes in the outer regions, which radiate and are registered as cooler atomic lines by the spectrometer during the later part of the plasma lifetime.

The experimentally measured emission profiles used to calculate the electron density are actually the result of the time-integrated blend of all the emission profiles present through the discharge lifetime; one can only characterise a grossly averaged plasma behaviour and as a result, subtle spark to spark electron density gradient changes may not be detected. If the temperature is calculated from a spectrum that is measured by integrating the intensity over a line of sight, it will be population averaged.

Furthermore, calculations for radiative plasmas are based on energy levels and dipole transitions rates of isolated atoms and ions. But when the density of the plasma is high enough, like in the sliding spark, the energy levels of bound electrons are shifted by the coulomb interactions with the free electrons, and some account for this phenomenon must be taken into consideration. Some levels can even be pushed into the continuum (pressure ionisation). When this occurs there is transfer of oscillator strength from line absorption to continuum absorption [136],which introduces errors in the values of the oscillation strengths used for the computations with far reaching repercussions on the value of the temperature obtained.

Mathematically, numerous plasma light sources, such as those associated with impulsing discharges, exploding wires, sparks, plasma jets, flares, laser-produced plasmas, may be classified as optically thick plasmas with a strongly inhomogeneous structure. The inhomogeneity is reflected in the spatial gradient of the temperature, the atom, ion and electron concentrations, and the variation of the intensity of the spectral lines. The inhomogeneity of an optically thick plasma is also reflected in the formation of strongly asymmetric self-reversed emission lines, together with asymmetric absorption lines having a deep trough in the middle and line wings. Resonance lines are commonly self-reversed and are of little analytical utility. Self-absorbed lines too cannot be used in accurate chemical analysis.

The optical thickness Γ of a flat layer of plasma is defined by [40]

$$\Gamma(\lambda) = \int k(\lambda) dl \tag{4.47}$$

where $k(\lambda)$ is the absorption coefficient at wavelength λ and the integral is taken over a finite path length in the direction of *dl*. Γ can be estimated from the ratio of intensities emitted parallel and perpendicular to the plasma layer by assuming a homogeneous plasma slab which is optically thin ($\Gamma \ll 1$) in the perpendicular direction and optically thick ($\Gamma \gg 1$) in the parallel direction. The thickness of surface discharge plasma can thus be mapped by plotting the integrated spectral radiances for selected line species above the substrate sample surface.

Most importantly absolute LTE, on which the temperature computations are based, cannot be assumed for a sliding spark discharge plasma. If the electron energy distribution function (EEDF) of a plasma obeys a Maxwellian distribution, the function would be Gaussian. However, due to high electron density, collective scattering has to be taken into account [186]. In general, all atmospheric plasmas with a radius of a few millimetres, will have a large gradient in the

electron density. This creates large losses of free electrons due to diffusion, which have to be compensated by ionisation.

To understand the physics and chemistry under the strongly non-stationery and non-homogenous equilibrium plasma conditions of the sliding spark in the temporal and spatial modes, a more detailed knowledge of the basic plasma properties is necessary, especially with regard to plasma column evolution and the properties of the ion and electron distributions. A variety of processes – electron impact ionisation, collisional transfers, recombination or chemical processes – result in the electronic excitation of the neutral and ionised species.

4.5 The Non-Equilibrium Effects

The temperature measurements computed and discussed in the previous section, among other considerations confirm that the thermal equilibrium basis for the derivation of in particular Eqn. 4.20 and Eqn. 4.22 is generally unfounded; all spark discharge plasmas depart from thermal equilibrium because there is always a flow of energy through the system.

In the recent years, it has become clear from experience in plasma applications that the Boltzmann distribution does not exist for all excited states. One must allow for other (non-Boltzmann) level populations. Nonetheless, spark discharge sources behave as if they were at very close to local thermal equilibrium (LTE), if any arbitrary small volume of the discharge is considered. There is a need - for precision - to use a different radiative model, which describes more accurately the relevant excitation and de-excitation processes, as they occur, for example, in the case of non-thermal equilibrium plasmas (also called cold plasmas) where the plasmas is a partially ionised gas at low pressure (0.1–10 Torr) but in which the electron temperature (20000–100000 K) is nonetheless much higher than the temperature of the atomic and molecular species in their neutral and ionic states (300–1000 K). These plasmas, electrically neutral at macroscopic scale, are produced in various types of electrical discharges, microwaves, etc., in the pulsed or continuous regimes.

The operational range of the electron density in a sliding spark plasma does not allow the application of corona equilibrium. Corona discharge is the first stage, however, of every discharge breakdown in inhomogeneous fields. Corona relationships mostly govern charge–state distributions in low density plasmas. For a plasma with low n_e , excitation by collisions is in equilibrium with depopulation by radiation, and the so-called corona model has a special solution for spectra of different ionisation levels n_z and n_{z+1} given by

$$\frac{n_{z+1}}{n_z} \approx 10^8 \frac{\zeta}{n_o} \frac{1}{\chi_z^2} \frac{\kappa T}{\chi_z} \exp\left(-\frac{\chi_z}{\kappa T}\right)$$
(4.48)

where ζ is the number of electrons in the atom outer shell; this shows that the temperature required for the appearance of a line is, in this case, considerably higher than in the case of thermal equilibrium.

The mathematical relations that accurately describe optically dense, non-equilibrium plasmas are complicated by various other factors.

The most major difficulty encountered is the solution of the rate equations, taking into account photon emission and absorption throughout the medium. One must resort to the physics of non-local thermodynamical equilibrium (nLTE) under the line transfer problem [187,188]. The principal equation describing the formation of emission line intensity in an optically thick medium is the emission transfer equation [189]:

$$dI_{v}(y,x)/dx = \in_{v} (r) - k_{v}I_{v}(y,x)$$
(4.49)

where $I_{\nu}(y, x)$ is the intensity of the emission at a frequency ν , leaving the source in the direction of the line of sight along the *x*-axis, located a distance *y* from the centre of the medium as depicted in Fig. 4.9. In the above equation,

$$\in_{\nu} (r) = \left(h\nu_o / 4\pi \right) A_{ij} n_i(r) P(\nu, r) \tag{4.50}$$

allowing for spontaneous transition, while

$$k_{v}(r) = \left(hv_{o}/c\right)P(v,r)(n_{i}(r)B_{ii} - n_{i}(r)B_{ij})$$
(4.51)

is the absorption coefficient. $n_i(r)$ and $n_j(r)$ are the concentrations of the emitting and absorbing atoms, respectively, while A_{ij} , B_{ji} and B_{ij} are the Einstein coefficients for spontaneous absorption and induced transitions, respectively, and P(v, r) is the local line profile.

The value of the intensity of the emission leaving a plasma can be taken as a solution of the emission transfer equation. This simplifies the calculations by enabling one to take into account a variety of factors affecting spectral line formation. From the extreme self-absorption, including self-reversals, it may be assumed that, in the general case, the emission zone of radius R_o of the discharge plasma is surrounded by an absorbing atom layer, in which emission is weak and may be neglected. However, no easy models can fully reflect the complex structure of an atmospheric pressure air plasma ablating a variety of atomic species from a non-conductor in all of its properties, especially concerning the broadening and distribution of the absorbing atoms.



Fig. 4.9 Geometric designation in the cross section of an axially symmetric plasma

First, instrumental response function (the response of the spectrometer to a δ -function-like emission spectral line) must be known accurately. The response function for a pulsed plasma discharge line may then be modelled by the sum of two equi-centred Voigt functions with different Lorenzian and Gaussian line widths and intensities to match the spectral line wings [190].

The main effect of a non-Maxwellian distribution is the modification of the rate of the various atomic processes in the plasma relative to a Maxwellian one. Non-Maxwellian electron velocity distributions in a laboratory plasma may be characterised either by enhanced or depleted high energy tail [191]. When a partially ionised plasma is in thermal equilibrium, the ionisation degree is well expressed by Saha equation. However, plasmas are in general not in thermal equilibrium. One of the fundamental problems of plasma-source spectrometry is predicting the ionisation balance. In order to obtain the ionisation degree in such plasmas, it is necessary to consider the various atomic processes. The ionisation degree as well as the population distribution of the excited atoms depend not only on the temperature but also on the electron state of the plasma, i.e., electron density [192]. The ionisation balance is controlled, in part, by the ionisation potential. The ionisation potential is reduced from the isolated atom value by interaction with the plasma. This ionisation potential depression (IPD) appears in the Saha-Boltzmann equation as $-\Delta \chi$ being the depression of the ionisation limit caused by the plasma environment, restricting the number of bound states available [193]. The calculation of the effective line contour shape is very difficult. An essential element complicating the solution is the desire to take into account the re-emission inside the plasma [194].

In the literature of atomic emission spectroscopy, the excitation energy of an ion line is often given as the sum of the ionisation energy of the atom and the excitation energy of the ground state of the ion to the upper level of transition. But ionisation and excitation are separate processes, since a collision that would remove one electron and raise another to an excited state is very unlikely. Excitation is described by the Boltzmann equilibrium. Ionisation on the other hand, especially for those excited levels that have principal quantum numbers greater than 1, cannot be governed by the Boltzmann relation, but by the Saha equation which describes the intensity ratios of the spectra of different ionisation levels; this takes either of the two forms:

$$\left(N^{+}N_{e}/N^{o}\right) = \left[2\left(2\pi m_{e}\kappa T\right)^{\frac{3}{2}}\mu^{+}/h^{3}\mu^{o}\right] \times \exp\left(-\Delta\chi/\kappa T\right)$$
(4.52a)

or

$$\log(N^{+}/N^{o}) = \log S + \frac{3}{2}\ln(\mu^{+}/\mu^{o}) - \log N_{e} - 0.4343\Delta\chi/\kappa T$$
(4.52b)

where N^+ , N^e and N^o are the numbers of singly charged ions, electrons, and neutral atoms per unit volume; μ^+ and μ^0 are the partition functions for the ion and atom, χ is the ionisation energy of the atom, S includes several constants, and the other symbols retain their previous meanings. This implies that the degree of ionisation is a function of electron concentration and temperature, which in turn is dependent on the position in the discharge column.

The above equations clearly reflect a modification in the partition function so that

$$\mu_{Saha}^{T}(T) = \sum_{n} \left(2J+1\right) \exp\left(-\frac{E_{i}}{\kappa T}\right)$$
(4.53)

where E_i is the energy of the state *i*, *J* is the angular momentum and *T* is the plasma temperature.

4.51 Autoionization and Collisional Radiative Transitions

The accurate interpretation of the observed radiative transition photon signals is only possible nonetheless if all interaction and transition processes are considered in the context of a collisional-radiative model. The atomic data, rate coefficients, transitional probabilities and lifetimes must also be known quite accurately in order to receive reliable results.

At low particle densities, most of the ions can be assumed to be in their ground states. The transitions between an autoionizing state a and the ionic state b can occur by means of the radiationless electron–capture and inverse autoionization process:

$$X^{+(z+1)}(b) + e^{-}(\varepsilon_i) \leftrightarrow X^{+z}(a)$$
(4.54)

considering the z and z+i times ionised levels X^{+z} and $X^{+(z+i)}$.

Autoionization processes leading to the formation of an excited state *i* following radiationless electron capture can provide a resonant contribution to the rate for the electron impact excitation of the transition $i \rightarrow j$.

Autoinonization thus plays an important role in atomic radiation processes associated with electron–ion collisions in high temperature plasmas, e.g., in the determination of the atomic level populations and the spectral line intensities of radiative absorption and emission in laboratory plasmas. In kinetic theory, autoionization resonances provide indirect contributions to the rates for excitation, ionisation and recombination [195]. There is a dynamic balance between the electron impact ionisation and the spontaneous radiative recombination.

On the other hand, stabilising transitions from an autoionization state *a* to a bound state *b* can occur by means of the spontaneous radiative decay process of frequency ω :

$$X^{+z}(a) \to X^{+z}(b) + \hbar v$$
 (4.55)

The two-step dielectric recombination process is accomplished through stabilising radiative transitions following radiationless electron capture.

These radiative transitions appear in the emission spectra in high resolution spectroscopy as satellites in the vicinity of a resonance line of the recombining ion. When the satellite features are resolvable from the associated resonance line, an analysis of the satellite and resonance line spectra can provide more precise information on the physical properties within the emitting region, such as temperature, density, and charge-state distribution.



Fig. 4.10 Elementary transitions involving autoionization states

In order to obtain the resonant contributions to the electron-impact ionisation rates, which arise from autoionization following inner-shell-electron collisional excitation, it is necessary to also take into account the inner–shell electron–impact excitation and de-excitation process:

$$X^{+z}(b) + e^{-}(\varepsilon_b) \leftrightarrow X^{+z}(a) + e^{-}(\varepsilon_a)$$

$$(4.56)$$

Since this process is important for the formation of the dielectric satellite lines, it should be critically considered in high electron density plasmas.

LTE is even more invalid when processes such as radiation escape or diffusion of particles are considered, or when collissional energy transfer between electrons and heavy-particles is inefficient (thus leading to generally two, transitional temperatures of the various species).

Table 4.2	Examples of the dif	ferent possible electronic inelastic collision, and radiative
	processes in an atmospheric pressure air plasma ⁴	
Collision dissociation		$AB + X \rightarrow A + B + X$
Dissociative recombination		$AB^+ + e^- \downarrow \Longrightarrow^2 A + B$
The collision attachment		$O_2 + AB + e^- \xrightarrow{1} a^2 O_2 + AB$
The Dissociative attachment		$O_2 + e^- \xrightarrow{1} e^2 O + O^-$
The direct charge exchange		$X^+ + Y_{-1} \rightleftharpoons^2 X^+ + Y^+$
Zeldovitch reactions		$NO + O_1 \rightleftharpoons^2 N + O_2$
		$N_2 + O_1 \rightleftharpoons^2 N + NO$
Indirect charge exchange		$NO^+ + N_1 \rightleftharpoons^2 N_2 + O^+$
		$NO^+ + O_1 \rightleftharpoons^2 O_2 + N^+$
		$NO + O^+ \xrightarrow{1} 2^2 O_2 + N^+$

At atmospheric pressure the temperature ranges in the sliding spark discharge plasmas seem to vary from between 2000 - 17000K. In these conditions the species that are important are free electrons, neutral molecules, their positive ions, and neutral atoms (both in ground state and excited energy states). Stein [157] developed a model to describe the behaviour of different neutral and ionic, atomic and molecular components of an air plasma at atmospheric pressure for temperatures lower than 4000 K under the influence of the non-equipartition of the kinetic energy and of the internal energy loses due to radiation escape. He found that at low

 $^{^{4}}$ X = O₂, N₂, NO, O, N.

temperatures, molecular dissociation does not result, especially for oxygen, from collisions between electrons and the neutral molecules in their excited states, but from collisions between heavy particles in the ground state.

Jacobs [196] showed that the presence of NO drives the air plasma constituents much closer to equilibrium than would be achieved in a plasma solely dominated by N_2 and O_2 . The negative molecular ions and atomic ions may be assumed to be in their ground state.

In the Collissional-Radiative (CR) model of the plasma, the number density, n_i , of each excited level of species *i* present in the plasma obeys a conservation equation (zero-order moment of the Boltzmann equation) in which the different processes leading to departures from LTE are explicitly considered thus

$$\frac{\partial n_{is}}{\partial t} + \nabla \left(n_{is} \left\langle \upsilon_{is} \right\rangle \right) = \frac{\partial n_{is}}{\partial t} \bigg|_{CR}$$
(4.57)

where the first term represents the temporal variation of the number density n_{is} , $\nabla(n_{is} \langle v_{is} \rangle)$ is the diffusion flux of species of mean diffusion velocity $\langle v_{is} \rangle$ and $\partial n_{is} / \partial t_{CR}$ stands for the variation in density due to collisional and radiative processes. The balance equation of the state *i* can be fully expressed as follows:



loss by charge exchange

 n_{ion} , n_e = density of ions, electrons, respectively. n_i , n_j = population density of the states i, j respectively. $\langle \sigma_{e,ij} \nu \rangle, \langle \sigma_{p,ij} \nu \rangle$ = rate coefficients for electron, ion impact excitation from state the state i to j respectively. $A_{i,j}$ = transition probability for spontaneous emission from state the state i to j. $\langle \sigma_{e \to ion,i} \nu \rangle, \langle \sigma_{p \to ion,i} \nu \rangle$ = rate coefficients from electron, respective ion impact ionisation, and $\langle \sigma_{ex,i} \nu \rangle$ = rate of charge exchange.

Fortunately for many applications, Eqn. 4.58 can be simplified. For instance, only for particle energies in the keV range are photon collisions and charge exchange effects appreciable. In a typical sliding spark discharge plasma the population of the excited states can be considered to

be small compared to that of the ground state, n_o , therefore $n_i \ll n_o$. As a consequence, the higher states can only be populated by electron collisions and depopulated into lower states mainly by radiative transitions. Accordingly, loss processes by collisions can be neglected; thus,

$$(3.59) (3.59)$$

But the observed emission signal remains dependent on the observation volume v, local density of the plasma discharge, electron density n_e , and excitation rate coefficient $\langle v\sigma \rangle_e$.

5.0 Instrumentation and Experimental Technique

5.1 Introduction

The basic principle of the sliding spark technique is the direct electro-thermal atomisation of a small amount of dielectric surface layer using high current sparks of defined discharge characteristics; therefore the pertinent question to ask is: can direct, quantitative spectroscopy be achieved in non-conductor matrices by use of the sliding spark, and if so, what are the instrumental and analytical conditions which influence heavy metal excitation in the sliding discharge plasma so that they can be moderated in order to achieve trace element analysis.

The first sliding spark spectrometry, which was developed by Golloch and co-workers [27] based on diode array detectors was utilised for the qualitative identification of plastics and fire retardant polymers based on the spectroscopic signatures from the reactive fillers, inorganic pigments and stabilisers that are normally embedded in these materials, and on [underlying] matrix-modulated spectra of the electrode material.

The technique demonstrated the potential for quantitative analysis when PVC and the thermoplastic fire retardants polymers were unambiguously identified on the basis of the atomic emission line intensities originating from the sputtered material from the copper electrode as a result of increased volatility in the presence of chlorine-containing matrix. Common additives in these polymers could be detected qualitatively, and quantification appeared to be possible if the matrix were known. Feasibility for quantitative work in chlorine-free samples was investigated [26,42] and found to be undermined by prospects of the effects of poor signal-to-noise ratios on the limits of detection even for light, easily ionised elements in their oxide form [197].

Although the kinetics of a multi-component, dense, open system such as the high temperature pulsed discharge plasma in air is very rapid and complex and therefore the mathematical formulation of any problem that aims at modelling the general chemical system is even more complicated (a predictive model for the sliding spark discharge plasma would need to give quantitative information on the chemical compositions of the matrix phases, the mass flux, the vapour pressure of the trace species, and the mass loss of the vaporised products in the course of the plasma evolution), a semi-empirical scheme that utilises metal oxides spiked in a halogen matrix to achieve high heavy trace metal spectral line excitation efficiency as enabled by the volatile halogenation process during ablation in non-conductor matrices is reported.

This chapter, which describes the sliding spark spectroscopy instrumentation, also outlines and describes the experimental technique, together with the methodological scheme adopted to investigate the analytical feasibility to directly excite, detect and quantitatively measure heavy elements present in non-conducting materials at trace concentrations when the sliding spark excitation is performed in air at atmospheric pressure. The resulting discharge plasma is fundamentally modified by use of a halogen-polymer simultaneously employed as both the underlying matrix binder and chemical modifier. Studies on the spectral characteristics of selected non-conductor materials of importance in solid-state analysis, excited in this way by the sliding spark, on the feasibility of the proposed methodology for typical samples, and on the evaluation of the potential of the technique for quantitative analysis, are presented.

5.2 Sediment as a Model Matrix

It was envisaged that if a sensitive method for the direct analysis of trace elements in non conductor materials is developed based on sediment as model matrix, it may be adapted to the characterisation of soils, sewage sludge, peat, fly ash, and several geo-environmental matrices. In principle, sediment, like fly ash on which the model¹ described by Chen *et al.* [198] is based, predominantly also contains CaO, SiO₂ and Al₂O₃ as the main matrix components.



Fig. 5.1 Sliding spark spectrum of a boro-silicate matrix bound in PVC, excited in air

¹ In attempt to develop a dynamic model for predicting the vaporisation behaviour of matrices containing both oxides and chlorides for application to the vitrification of fly ash, Chen ad co-workers found that to extract the heavy metals by vaporisation, low oxygen partial pressure and high temperature are necessary; chlorides favoured the vaporisation of heavy metals, especially at high oxygen partial pressures. In discharge plasmas, the operating conditions of oxidising or reducing atmospheres are also known to modify the volatility of heavy trace elements.

In Fig. 5.1 a test spectrum excited by the sliding spark directly, from a simulate boro-silicate $(SiO_2+B_2O_3 \text{ mixture})$ bound in PVC (in a 1:1 ratio) under both 'soft' and 'hard' discharge conditions, is shown.

The spectrum in Fig. 5.1, whose various spectral peaks can easily be assigned to their emitting species, demonstrates the ability of the sliding spark technique to not only successfully excite the lines of the tungsten electrodes and the major constituent elements in a typical geological sample including the binder modifier, but also the potential to combine source parameter modulation and halogen volatilisation to develop a method for quantitative analysis. The Si I 251.611 line for instance is measurable under 'soft' but not under the 'hard' discharge condition.

The remainder of the species lines indicated in the Fig. 5.1 including B I 249.773, have intensities that depend on the excitation source parameters responsible for the discharge hardness, i.e., the sliding spark source circuit current, capacitance and inductance. It is thus, in principle, spectroscopically possible to directly analyse using the sliding spark technique, complex geological, including other environmental matrices for the various elements by modulating both the instrumental parameters and the sample matrix to be analysed.

The choice - and characterisation - of sediment as a model non-conductive solid matrix is based on the fact that the direct examination of sediments for multi-elemental information represents an important field of activity in instrumental analysis but which is still faced with complications that arise from how the physical and chemical properties of sediment couple with the environmental and geochemical observables, e.g., particle size, geochemistry, and matrix composition. The physico-chemical properties - and thus indirectly the geochemical composition - determine the size and distribution of the trace natural minerals in sediments. There is a particularly critical relationship between particle size and sediment geochemistry.

One of the major problems in solid state [plasma-source] spectroscopy that demand careful study is particle-plasma interactions; these give rise to spectral line interference [and other matrix] effects which are influenced by size and the chemical composition of the matrix particles. Analytically, the sediment matrix is [ideally] highly inhomogeneous.

Like all geological samples sediment also contains refractory minerals such as spinnels and alumino-silicates, which are not readily decomposed [199]. Since the sliding spark technique involves thermal processes for the particles generated in the discharge plasma, the constituent minerals of sediment are expected, during the atomisation processes, to undergo complex selective ablative vaporisation resulting in different volatilisation and thus, species excitation rates: a careful study of these mechanisms could lead to a better understanding of how to manage

representative ablative sampling, trace elemental excitation efficiency, the control of matrix effects, and the search for a suitable calibration strategy, is necessary not only for sediment analysis but also for the analysis of other refractory solid materials.

In direct solid analysis the amount of sampled material is governed by the natural homogeneity and texture of the matrix and the traces distribution. The applicability of quasi-direct solid analysis techniques, for instance slurry sampling, to sediments, is, strictly speaking, not analytically viable because the requirement of single phase powder does not exist: the slurry technique requires not only much more sample material than does direct solid analysis, the sample must also be homogenous and form a stable suspension of powder during the dosage procedure [21]. Direct sample excitation has the advantage of furnishing analytical data without loss of time.

Although the most important element in sediment, silicon, is also available in a wide variety of matrices including natural samples as well as industrial products (it is the second most abundant element in the earth's crust, and is widely used in industry and commerce [200]), essentially, the sediment matrix consists of a complex mixture of the geochemical phases quartz, plagioclase, k-feldspar together with chlorite, amphibole, and mica. These phases include carbonates, sulphides, inorganic and organic carbon matter, iron and manganese oxides, which together with the carbonates, sulphides and iron and manganese oxides may occur in a variety of structural forms that act as reservoirs for heavy trace metals [201,202].

As a consequence of the contamination of soils from various anthropogenic sources (e.g., fertilisers, sewage sludge, manure, pesticides, atmospheric deposition), the concentration of heavy elements in the sediments changes continuously and the levels often far exceed the original concentration formed by weathering of the parent material. For instance the wide use of fertilisers in certain regions has been identified as responsible, albeit marginally, for Cd pollution. Due to acid-mine drainage and industrial waste dumping, estuary, reservoir and river sediments < 63 μ m may [also] contain elevated levels of Cu, Zn, As, Pb, Mn, and Hg. Atmospheric deposition normally contributes to pollution due to the elements Pb, As, and Hg.

Hakanson and Jansson [203] have observed that differences in sediment parameters, such as organic content and mineral matter may markedly affect their concentration of trace elements. The reason is, elements in sediments are not primarily in 'solution', but are attached to various carrier particles i.e., suspended organic and inorganic aggregates of different origins and chemical character. Organic ligands, for instance, bind - and therefore modify the toxicity - of the trace metals. Sedimentary organic material plays an important role in regulating the metal

concentrations. Sediments that contain high components of smectic clays (as compared to illicit or kaolin) can bind and accumulate significant amounts of heavy metals [204].

The general composition of clay minerals - which is the most important constituent of the very fine part of the sediment - is about 30 % Al_2O_3 , 60 % very fine SiO₂ and 10 % other elements the most dominant of which are Na, K, Ca. K is mostly found in chlorite clay [(Mg, Fe, Al)₆(Al, Si)₄O₁₀(OH)₈], K-feldspar (KAlSi₃O₈), illite, smecite, and mica (mostly muscovite and biotite). The various metal constituents present in the sediments have a differential distribution in the several different mineralogical phases.

From the literature, sediment samples from lakes, ponds, rivers, reservoirs and oceans have received great interest from the viewpoints of geochemical, paleontological and environmental science because they are a continuous repository of geological and environmental change. Release of the sediment-bound heavy metals can have a significant influence on the water quality: variations in the environmental physico-chemical conditions can mobilise the heavy metals [205]; this allows these metals to re-enter the overlaying water, resulting in their increased bio-availability. Bottom sediments are especially carriers and potential sources of contaminants in aquatic systems, so they can affect the groundwater quality and agricultural products when disposed of on land. The chemically active fraction of sediment is usually cited as that portion which is smaller than 63 μ m, i.e., the silt + clay fraction; it is the primary carrier of adsorbed chemicals, particularly phosphorous, chlorinated pesticides and most heavy metals.

While spatial geochemical trends relate to the natural and anthropogenic sources of the sediment from a number of geologically contrasting basins that contribute to the elemental concentrations in the sediments, the spatial trace elemental concentration distributions in receiving waters reflect the textural and mineralogical transitions within the reservoirs and tributaries of the source rivers and streams [206].

The type of carrier particle and the manner in which elements are bound to it in the sediment, therefore, determine the element's geochemical fraction in the matrix. Although the ultimate sink for the elements in solution is the bottom sediment [207], trace elements that enter into the aquatic systems tend to be sorbed onto the sediments. No simple, uniform model is available to describe the sorption intensity and capacity of heavy elements in sediments. The difficulty of assembling such a model lies in the fact that while a variety of sediment constituents e.g., clay, iron oxyhydride, manganese oxyhydride and organic matter can sorb or affect the sorption of metals, the composition and structure of natural sediments are extremely complex and diverse, i.e., site-specific. While clay minerals alone in aqueous solution can strongly sorb trace metals in

sediments, their surfaces may be masked by iron and manganese oxyhydrides [208], providing little access to sorbed trace metals.

5.3 Sliding Spark Spectrometry Instrumentation

The sliding spark spectrometer (Fig. 5.2) consists of four functional groups:

- high voltage spark generator
- measuring gun (spark source)
- spectrometer optics with 3 CCD detectors coupled together;
- industrial PC with control and measurement electronics.

The spark source, which is enforced by the geometrical orientation of the electrodes to rest a small distance (≈ 4.5 mm) apart across the surface of the underlying dielectric matrix, generates the spark, which slides over the surface of the material that is also the analysis sample. The electrodes are composed of tungsten, chosen for its high corrosion resistance, high melting temperature, and low ablation propensity in order to suppress any characteristic radiation from it that would cause severe spectral interference with the analysis lines of interest excited from the matrix sample; in principle one may not analyse the same element spectral lines as those of which the electrode material is made since spectral interference in the wavelengths chosen for the analysis.

The spark is brought about by a high voltage pulse from the ignition process. The ignition voltage increases linearly to a level of several kV within a few (~ 6) μ s. The idea is to initiate an abrupt collapse of the high voltage, which masks the breakdown of the discharge across the base matrix. The maximum voltage immediately prior to the breakdown of the spark gap, and its evolution in subsequent breakdowns represents a [matrix-dependent] pattern.

In the course of the sequence of the spark discharge process, the surface of the material is changed in a specific manner; the continuous dissipation of energy along the sliding spark leads to the removal of the material (crater formation) or incrustation of the sample surface whose progress in terms of the surface breakdown voltage provides a further parameter: a semiquantitative descriptive model of the surface discharge propagation in vacuum makes it possible to determine the electrical strength and voltage at which the streamer discharge arises in the vicinity of the surface, and a material-specific function, known as the Dynamic Disruptive Discharge (DDD) voltage, can, in a time-resolved mode, be measured for each element line as a function of the spark sequence to provide a further characterisation parameter of the sample matrix being analysed.



Fig. 5.2 Schematics of the sliding spark spectrometer



Fig. 5.3 The integrated sliding spark spectrometer

In order to minimise the attachment of loose particles to the analysis sample, during the sparking process a vacuum pump sucks the vaporisation products out of the sparking chamber via a course particle filter through a filter cartridge packed with activated carbon. A protective capacitive proximity switch integrated in the measuring gun prevents sparking on conductors. The complete spectrometry (AGR, Essen, FRG) system is integrated in the housing modular fashion (Fig. 5.3).

The radiation generated by the sliding spark on the sample surface layers is focused by a quartz glass optical fibre of high UV transmission and large acceptance angle, and transported to a multi-channel spectrometer for wavelength dispersion on an imaging diffraction grating. Fused fibre transmission techniques are reviewed by Siegmund [209]. The geometry of the lens-fibre system is optimised to subtend the widest possible solid angle of view to the quartz lens and radiation transmitting optical fibre. Attention to detail in mounting the experimental set-up of the optical fibre system is essential if the optics is to perform optimally. Key characteristics that have to be considered include:

- (a) Numerical aperture
- (b) Fibre seize and bundle size
- (c) Extra mural absorbance
- (d) Core to cladding ratio; and
- (e) Shears, defects and gross distortion

A single fibre in a fused fibre optic consists of a core glass of index of refraction N_c surrounded by a lower index N_s , glass' cladding.



Fig. 5.4 Schematic representation of light transmission in an optical fibre²

² An optical fibre of index of refraction, N_c , and cladding of index N_s , will accept incident light from a material of index N_A according to Snell's law: $N_c \sin \theta_c = N_c \sin \theta_c$. Light will propagate down the fibre provided there is total internal reflection at the cladding interface




Fig. 5.5 The spark head showing the orientation of the electrodes with (a) a sliding spark propagating across them in air and (b) view of the optical fibre and quartz lens

By Snell's law, light incident upon the core from material index N_A will propagate along the fibre by total internal reflection as long as the angle of incidence to the core is less than $\theta_A = \theta_{\text{max}}$, given by

$$N_{A}\sin\theta_{\rm max} = \left(N_{c}^{2} - N_{s}^{2}\right)^{\frac{1}{2}}$$
(5.1)

The numerical aperture (N_{Ap}) is the sine of the half-angle of the acceptance core and simply equal to sin θ_{max} , when the incident medium is air, i.e., when $N_{Ap} \approx 1$ [210].

5.4 Spectral Dispersion

The sliding spark spectrometer consists of a holographic blazed grating optical system, which scatters the spectrum and isolates the analytical lines of the excited elements under study.

Because the overall performance of a polychromator essentially depends on features such as brightness, stability, spectral purity, quality of the grating grooves, band pass, and resolution, selecting spectrograph grating for an analytical spectroscopy application is best realised by considering the following parameters:

- the grating groove frequency;
- the spectral range;
- the size of the grating;
- the blaze wavelength;
- the distance from grating centre to the entrance slit;
- the distance from the grating centre to the first point on the detector;
- the distance from the grating centre to the second point on the detector; and

• the angle of incidence.

These parameters can be selected, designed or modified for the spectroscopic grating that suits specific applications. The shortest wavelength transmitted for most systems is ≈ 180 nm.

Until recently almost all spectrometer instruments with concave gratings were based on the Paschen Runge polychromator technique, which consists of an entrance slit, a [concave] grating and exit slits.

In the work reported in this dissertation a linear array of three CCD detectors was used, therefore the Rowland circle arrangement was not necessary. The idea of having a compact system that is portable and which can be used for field analysis in the future, necessitated the use of short focal length of the optical dispersion system.

This was achieved by resorting to the use of a blazed holographic grating with sinusoidal grooves. The entry slit width was selected to achieve the band pass and spectral resolution that is sufficient. Table 5.1 summarises the technical data of the entire CCD spectrometer system used for the spectral detection. The schematic of the dispersion system is shown in Fig. 5.6.

Grating	Holographic blazed grating					
Grating constant	1600	grooves/mm				
Focal length	150	mm				
Diameter	20	mm				
Blaze	220	nm				
Blaze angle α	5	0				
Entry slit width	11 & 35	μm				
Reciprocal linear dispersion	4.2	nm/mm				
Wavelength range	212 - 511	nm				
3 CCD-(2100 pixel) sensors	UV sensitised one-dia	mensional array				
Pixel Dimensions (W x H)	14 X 200	μm				
Dark current @ 293 K	0.3	mV				
Operational voltage	1.8	V				
Dynamic range	6000					
Total transfer efficiency	95-97	%				
A/D conversion	12	Bit				
Dimensions (L x W x H)	20x15x10	cm				

 Table 5.1
 Technical data of the CCD spectrometer employed in the measurements



Fig. 5.6 The principle of detection by CCD spectrometer³

5.41 Photon Detection by Means of CCD Detectors

Traditionally, spectroscopy has involved using a scanning monochromator and a single element detector (e.g., silicon photodiode, photomultiplier tube, etc.) placed at the exit slit of the dispersion system. In such a set-up, a complete spectrum is built up point by point, by moving the grating to select each wavelength.

By contrast, in multi-channel spectroscopy the grating is fixed, while the exit slit and single detector are replaced with an array of detectors, each viewing a different wavelength. Typically, one kilobyte (1024) 26 μ m or two kilobyte (2048) 14 μ m detectors are used, and a complete spectrum is recorded in the same time it takes to record one wavelength point with a scanning system.

A sequential (scanning) instrument contains a monochromator that scans the spectrum, pausing at each analytical wavelength long enough to achieve a desired signal-to-noise ratio. Array detector-based spectrometers have better stability and reproducibility since they have no moving parts. These (multi-channel advantage) properties have been exploited in sliding spark spectrometry.

³ A: Entry slit B: Optical fibre, C: Grating, 1,2,3: the detection CCD sensors array.

Because of the long discharge duration (25-1000 ms) used in the electronics of the present design of the sliding spark spectrometer, the amount of data collected during a typical discharge is in general huge. The utility of multiple channels allows the possibility to monitor variations in the species concentration within the discharge column resulting from elements embedded in the matrix based on multi-spectral information (for sensitive quantitative analysis there is a necessity for good temporal resolution).

When there is a fundamental desire to develop a sensitive detection system for analysing spectral data, for instance from excited trace element species embedded in the surface layers of a dielectric matrix excited by a typical pulsed surface discharges which aims to achieve high temporal and spatial resolution, the CCD detector technology can enable the acquisition of relevant optical data which can give insight into those spark processes that are important in quantitative analysis. The CCD detectors are well suited for the task of detecting, within a relatively short time, the weak photon signals, because CCD detectors possess a high quantum efficiency for converting photons into electrical signals even at room temperature.

The CCD detectors also have sufficient resolution, which in conjunction with the appropriate computing interface - which includes in-built electronic FET switches needed to read from individual pixels - provides multi-element analytical capability with low background, good linear dynamic range, line selection after data acquisition, wide spectral response, and a cross checking for linear overlaps; all these properties are well suited to analytical spectroscopic applications where there is plenty of signals - the additional resolution given by the smaller pixels is a benefit especially for applications such as beam profiling and monitoring where the read-out speed is critical.

A CCD is essentially a one or two dimensional solid–state silicon-based memory array photo sensor like the PDA (photodiode array). A CCD is however 100X more sensitive than a typical PDA, making it the detector of choice for low photon yield sensing such as in trace element analysis in high background matrices, in Raman scattering, or low quantum yield luminescence. The readout mechanism for a CCD differs significantly from that of the PDA.

Typically, a CCD has a sensitivity similar to that of a photomultiplier tube; however, unlike the photomultiplier tube, the CCD is not damaged by over-exposure to radiation. Detailed physical description of CCD detector arrays relevant to analytical spectroscopy (the actual physics is more complicated) are among other literature addressed elsewhere [211-213].

At the heart of all CCD detectors is a light-sensitive metal oxide semiconductor (MOS) capacitor, which has three components consisting of a metal electrode (or gate), an insulating

film of silicon dioxide, and a silicon substrate. MOS capacitors are segregated into two classes of devices, one having a surface channel structure and the other having a buried channel design. It is the latter device that is used in the fabrication of modern CCDs detectors due to several advantages of the buried channel architecture. The MOS capacitor array is fabricated on a p-type silicon substrate (illustrated in Fig. 5.7) in which the main charge carriers are positively charged electron "holes". Prior to the multi-step photolithography-driven CCD fabrication process, a polished silicon wafer is bombarded with boron ions to create channel stops that localise integrated charge within the confines of a single pixel gate.



Fig. 5.7 The diode structure of a CCD illustrated by a schematic drawing of the potential well based on the MOS capacitor

After the buried channels are formed within the silicon substrate, a layer of silicon dioxide is thermally grown on the silicon wafer surface to provide an insulating base for the gate electrodes. Next, a phosphorous-doped layer of polycrystalline silicon (polysilicon) about 5000 Å thick is grown on top of the oxide layer. This layer of polysilicon comprises the gate electrodes and is transparent to visible light, making it an ideal substance for use in CCDs. Although the fabrication of a complete CCD takes additional steps, the basics of the MOS capacitor assembly are basically complete at this point.

When light strikes a CCD pixel, electric charge builds up on the device; the amount of charge is directly proportional to the number of photons (or intensity) at that point of striking for each pixel. The charge build-up is monitored electronically: on a CCD, each pixel is overlaid with a

small voltage-carrying element (electrode). During the illumination of the entire chip, the charges generated by light accumulate in the pixels, specifically in the potential wells beneath each pixel. The charges may be "welled" down the columns by an appropriate sequence of voltages clocked on to the electrodes.

The CCD readout consists of a charge transfer scheme whereby the entire charge is moved down a row with the last row being shifted into the serial register (parallel read out mode). All columns terminate in an output analogue shift register. The output of the pre-amplifier is proportional to the charge shifted on to the output gate, where it is digitised for computer processing. Digitised pixel values are output from the pairs of the differential lines, controlled by dedicated software.

All the pixels are dumped into the CCD in one cycle of the transfer gate. How often the pixels are dumped and the CCD emptied depends on the light level and on the speed with which the light source changes. CCD detector outputs are normally digitised at specified bit/pixel by customised electronics that use a specialised ADC circuit, which permits image/photon acquisition rates up to predetermined frames at a specific resolution depending on the spectroscopic application.

The CCD read-out can also operate in the pixel transfer (serial read out mode); here each pixel is clocked out serially from the serial shift register - by masking out all but a single row of the CCD, one can also clock the device (with no frame enable clock). The most significant benefit of this readout method is that the readout noise is very low.

The clock electrode and SiO_2 dielectric are like the gate electrode and insulator in a MOSFET. To collect the charges as data signals, an appropriate sequence of voltages is electronically clocked across the electrodes to 'well' the charge row by row down the vertical dimension of the chip into a shift register at the bottom of the array.

To fabricate the channel stops of the CCD, a portion of an insulating material, such as Si_3N_4 layer, is etched away. A P⁺ dopant is then implanted into the bulk primary silicon material of the detector.

Finally, the silicon is oxidised to create an insulating layer of SiO_2 between the channel stop and the gate structure. The gate structure is then grown on top of the silicon after this process. The sub-pixel structures include the polysilicon gates and insulating layers, as well as channel stops, the implanted P⁺ channels and their insulating layers.

The transfer gate electrode functions much like the gate in the CCD. When the transfer gate goes high the photoelectrons are attracted to the gate region. Just as in the case of the CCD gate there is non-uniform doping hence when the gate goes low again the photoelectrons are dumped into the CCD rather than returning to the P region.

Where as readouts in the CCD are all ADC-limited and at 65 K, the CCD is nowhere near saturation, which occurs at about 450000 e-/pixel. A typical CCD is characterized by a specified full-well capacitance of the order of 10^5 e⁻. Some, instead, are limited to a maximum of about 35 K ADU because of the saturation of the electronics amplifiers ahead of the DCS stage.

All CCDs may be used at a range of readout speeds - with trade-off that shorter read-times mean larger read-noises. Regardless of the read-out technique employed just two clocks are sent, namely a charge transfer and serial transfer clocking. The time resolution achieved in the serial readout mode is typically serial clock frequency (~10 mHz) times the number of serial pixels. Thus, several tens of thousands of row scans can be obtained with time resolutions between 50 to 100 μ s/row. These novel, serial and parallel readout schemes, may be exploited to allow one to use them as a linear array with much improved time resolution. One can send up to 500 - 1000 image transfer pulses, and use the rest of the CCD as a storage device. In such a readout scheme, a time resolution on the scale 1 - 2 μ s/row is obtained, with the number of single row data frames limited to that of the rows in the CCD.

When operated in frame-transfer mode, photo-charge integration time amounts to 96 % of the inter-frame interval; in this case during the remaining 4 % of the time pixel data are shifted from the photon-exposed to the masked region of the CCD. The two schemes may each be utilised depending on the nature of the spectroscopic application.

To improve the sensitivity of the CCD in the blue-visible and UV wavelengths, a composite coating may be used [3]. This treatment achieves a dramatic increase in device sensitivity in the 120–430 nm wavelength range - this region is where most of the analytically useful lines are detected in sliding spark spectrometry. The sensitivity is improved equally for both front-illuminated and back-illuminated CCD.

5.5 Spectral Signal Acquisition and Noise

The overall noise associated with the acquisition of spectral maps by a CCD device are, readout and the dark-charge noise respectively, and the photon shot-noise associated with the emission signal. The consideration of noise is a very critical subject in analytical spectroscopy [214]. If a typical CCD is illuminated to half-saturation under constant and uniform conditions without

cooling, the single-pixel noise, measured during sequence acquisition at the maximum frame rate, can be approximately 2.5 bits.

As the photon shot noise is the square root of the number of photoelectrons, the contribution to the overall noise from the electronics is of the order of 300 e⁻, a figure that is due almost exclusively to read-out noise and therefore can be assumed as the upper-bound for the electronics noise at all operation rates. In fact, read-out noise decreases where as dark current increases when reducing the speed of acquisition, but leakage current can be kept efficiently under control by cooling the detector.

The CCD, like all detectors, also has a leakage current, often called the dark current. The dark current adds to the photon signal of interest and that has important consequences in sensitive trace element analysis beyond the simple requirement to subtract dark charge from every signal reading; it sets a limit on the exposure time for each measurement since charge saturation is fated to occur.

Because dark current varies with temperature it does not only contribute to the noise, it can cause baseline (background) changes over time. Due to the exponential dependence of temperature on the dark current (it halves for approximately every 7 $^{\circ}$ C drop in temperature), the problems associated with the dark current can only be minimised but not eliminated by cooling. Cooled systems in any solid-state detector greatly extend the maximum useful exposure time by reducing charge build-up due to the dark current. A typical CCD has its highest performance in cooled systems that use efficient thermoelectric coolers inside an evacuated housing; in that case, no external power supplies, water or liquid nitrogen cooling like for the case of Si(Li) detector are required. The contribution from the dark current to the total noise becomes negligible for frame rates down to 50 frames/s when the CCD is kept at 15 $^{\circ}$ C - approximately at room temperature.

5.6 Data Processing and Transfer

In the present sliding spark spectrometer, three CCD detectors register and measure the dispersed spectrum. Approximately 6300 pixels of the optical spectrum are scanned simultaneously across a wavelength range 212 nm $\leq \lambda \leq 511$ nm with a spectral resolution of ≈ 0.05 nm. (Only when the radiation emitted from the plasma is adequately spectrally resolved, can the trace analyte species in the solid underlying matrix be identified and quantified by their unique wavelengths and line sensitivities). The CCD output, which comprise both spectral line and the DDD data, are read opto-electronically after each sparking process. Both the CCD and the DDD data signals are digitised on an interface board and transferred to the evaluation computer.

To improve on the signal-to-noise ratio, the signals are accumulated by the software after each individual sparking process and are then arithmetically meaned by the number of measuring scans, which can be set via the software to give the spectral representation that follows. The first one spark shot may not be integrated, if it is utilised as a cleanser spark to remove any possible sample surface contamination due to adsorption. An industrial PC with (PC/104 technology 6.5^{''} TFT) flat screen, which also supports external serial interface is used to transmit the sparking parameters to the high voltage spark source and the spectrometer electronics. The PC also processes and evaluates the acquired signals directly. For instance, the duration of charging process of the pulse capacitors in the spark source and thereby the amount of energy stored, in them, among other parameters, can be set via the software. A direct operating of the software is made possible with an integrated 8 x 8 matrix touch panel.

The application software provides for the possibility to enable the spectrometer read and record photon spectra, which do not originate from the sparking process online. This provision was used to perform the spectrometer calibration. Owing to the laborious nature of the calibration procedure in sliding spark spectrometry but which is nonetheless the most important aspect and thus must be done to the highest accuracy attainable, numerous hollow cathode lamps with emission wavelengths selected for this task spanning the entire analytical region of interest, were utilised. Each CCD was first calibrated separately, then the three CCDs used were re-calibrated assumed to be coupled as one. The calibration was refined by use of high purity oxides and chlorides of selected elements with known high emission cross-section in the visible ($\sim 400-700$ nm) and UV ($\sim 200-400$ nm) spectral range⁴.

No radiation was measured below 210 nm; optical fibres have a low transmission efficiency below 200 nm. This region (VUV: 40–160 nm) however contains the strongest lines of particularly the non-metal elements C, P, S; these were not of interest in this work, which focused mostly on the quantitative investigation and evaluation of the heavy metals.

5.7 Test Sample Preparation and Analysis

General requirements of calibration materials for micro and trace analysis are that, they primarily have a matrix that matches the samples to be analysed, both chemically and physically, and that they have good homogeneity on the small scale of resolution on which the technique operates. It is usually unrealistic to expect to find natural materials that satisfy these requirements. In the

⁴ While theoretical work requires and even lists wave numbers in vacuum, it is necessary to convert between wavelength in air and vacuum, thus λ_{air} (Å) = 10⁸/ $\eta \mathcal{G}$ (cm⁻¹), where η is the refractive index in air, and \mathcal{G} is the wave number, which should in practice be added in order to obtain an accurate calibration of the spectrometer and the assignment of the detected spectral lines.

case of the sliding spark technique, particularly for very rough or porous samples, the conditions required to maintain a stable discharge plasma are difficult to attain.

Since it is well known that the ablation rate and atomisation efficiency in a pulsed discharge plasma on surfaces are dependent upon the particle seize and morphology of the matrix surface layers, to minimise the influence of different grain seize on the sparking process and on the particles reaching the sliding spark plasma, the grain size parameter was controlled during the sample preparation process.

Only samples of finely-milled powders of PVC and the other candidate matrix binder modifiers - cellulose, teflon, borax, together with high purity oxides of the elements Fe, Ni, Cr, Cu, Pb, Zn, Cd, Hg, As, Al Co, Ti, V, Mn which were also spectroscopically investigated with the aim of developing a scheme for the analysis of simulated and analytical sediment, were used. As laid down by national (Germany) and international monitoring programs, the first ten elements listed above are required for routine measurements in sediments; Co, V, Ti, Mn may be of additional analytical interest.

A representative portion of sample was entirely reduced to a smaller grain size with a tungsten carbide disc mill in a Spartan 3 (Fritsch, FRG) pulverizer. In order for the materials to have as similar grain size as possible, they were not milled too much, the aim being for most of the particles to be $< 90 \ \mu m$ and $> 20 \ \mu m$. The powdered materials were screened to pass through a 60 μm aperture sieve (250 mesh) and to be retained by a 20 μm -aperture sieve (625 mesh). The samples were then briquetted into 28 mm diameter pellets of good mechanical stability weighing about 4 g, at 600 kN pressing force, in a small laboratory press (Herzog, FRG). A pressing time of about 10 minutes for each pellet was observed in order to ensure some kind of reproducibility in the sample compatibility and mechanical stability.

The oxides of the elements under investigation (with the exception of CoS which was also additionally studied; for Mn and Ni the carbonates were also studied) were used in the analytical scheme. This was done in order to match as realistically as possible the natural form in which the elements to be investigated exist (i.e., the elements are embedded in the sediment mostly in the form of oxides or carbonates) and thus are to be measured in final quantitative analysis using the sliding spark technique after the calibration strategy is developed. It is also essential to develop a measurement procedure based on a particular class of compounds for all the elements since the atomisation and excitation efficiency of elements in any solid matrix excited by the pulsed discharge plasma depends on the form in which the trace elements are bound. The matrix composition of analysis samples has a strong influence on the atomisation processes and thus the calibration strategy adopted in sliding spark analysis. Spark excitation efficiency depends on

matrix composition as a result of thermodynamic considerations. The use of the oxides samples thus not only provides access, through sliding spark excitation, to the most likely form in which the elements exist in the natural sediments; in addition, it is also the best way in which to study the most easily ionised elements and thus to obtain basic information on the role of discharge parameters on atomisation and ionisation of these elements in the sliding spark discharge plasma.

Element	[I] oxide	[II] oxide	[III] oxide	[IV] oxide	[V] oxide	[VI] oxide
Ti						
Fe						
Cu						
Со		[S]				
Mn		[CO3]				
Cr						
V						
Pb						
Hg	[C1]					
Zn						
Cd						
Al						
Δs						

Table 5.2List of elements used in the analysis scheme. Except otherwise indicated the
elements were in oxide form with the respective states denoted by the shades

The studies described in this chapter based on these elements are preliminary measurements which focus on the atomisation and sliding spark discharge radiative characteristics of the elements excited as oxides embedded in the various non-conductor matrices. Where applicable more than one ionic state of the excited elements as they occur in oxide form were compared to investigate whether spectral line occurrence patterns of the elements are a function of the valence state of the oxides; this information is essential if sliding spark spectrometry is to be developed for speciation analysis in environmental matrices.

[CO3]

Ni

The methodological approach involved testing the spectral response of both major and trace elements spiked as oxides in a test PVC matrix; the excited and measured lines were assumed to be the same lines that are able to be observed and measured in both a simulate, and the real sediment matrix.

The purpose of binding the oxide test samples in a PVC matrix was to investigate the influence of halogen polymers as both sample binders and matrix chemical modifiers in sliding spark spectrometry. It was observed, as is already implicit in Fig. 5.1, that a halogen-based polymer simultaneously employed both as a chemical modifier and sample matrix binder improves the excitation efficiency of the trace elements as a result of the increased atomisation through formation of volatile halides in the sliding spark discharge plasma.

This property is better demonstrated in Fig. 5.8, in which a 33 nm wide spectral window in the UV regime is scanned for the various non-conductive sample binders that may be used in sliding spark spectroscopy analysing powder samples. The matrices were excited under same spark source parameters at atmospheric pressure in air. Pure grade (99.95 %) samples were employed in these tests. The spectral window was observed to contain a number of excited [major element] lines.

The characteristics of the measured spectra in the spectral window shown in Fig. 5.8 and the entire spectral region accessed by the technique for the test matrices demonstrates that, firstly, sliding spark spectrometry accomplishes the direct excitation of a variety of non-conductive solids with an excitation efficiency that is matrix-dependent. For instance, borax $(Na_2B_4O_7.10H_2O)$, a purely inorganic matrix, in spite of being composed of the easily-ionisable elements Na, B, shows the least spectral responsivity as observed from the height of the measured peaks and the baseline (background) structure, while teflon shows the highest.

It is noted that the most sensitive line of boron, B I 249.773, which has a first ionisation energy of 8.296 eV, can be excited in the borax matrix. In the event thus, that the atomisation and excitation is not aided by enhanced volatilisation resulting from the use of a halogen matrix modifier, major element concentrations of easily ionised elements in non-conductor solids may be measured directly with a good signal-to-noise ratio using sliding spark spectrometry operating in air at atmospheric pressure.

For the carbon-based matrices - cellulose $((C_6H_{10}O_5)_n)$, teflon $((CF_2)_n)$ and PVC $((CH_2=CHCl)_n)$ – which have respectively the ratios 2:5, 1:2, 2:5 of carbon: x (where x stands for the other atoms in the molecule), it may be observed that the most sensitive ionic line of carbon, C III 229.687, is the highest measured carbon line intensity in the teflon matrix, followed by cellulose, then PVC and lastly borax where carbon can be assumed to occur at trace concentration albeit with measurable intensity (as can be observed in the spectrum) – an indication that trace metrology is feasible in sliding spark spectrometry.

However this result is not exactly corroborated by observing the intensity of the spectral lines CII 251.206 and C II 274.728. Both thee lines are not sensitive carbon lines. The observed intensities of the same lines is much higher in the teflon matrix. Meanwhile the line intensities measured in cellulose and PVC are equal. This result seems to suggest that it is the ratio of the halogen to the carbon directly, rather than that of the halogen to all the other constituent atoms of the molecule, which plays the critical role in influencing the degree of elemental atomisation (excitation) as a result of halogenation. It should be noted that the ratio of carbon to the rest of the atoms in the molecule is the same in both cellulose and in PVC.

Although the above result may also partly be explained based on the assumption that the more volatile fluorides favour excitation in the discharge plasma of teflon matrix, as compared to the chlorides in the PVC matrix, the ratio of carbon to the rest of the atoms in the molecule, which has a direct bearing on the relative abundance of the element being measured, ought to be also taken into account when comparing the carbon line intensities of the halide matrices.



Fig. 5.8 Typical spectra of the various dielectric matrix binder/modifier candidate materials for sliding spark spectrometry excited by the sliding spark in air at atmospheric pressure

A different picture emerges still when the neutral line C I 247.856 is considered. The C I 247.856 is one of the sensitive lines of carbon; for this line the measured intensities in all the three organic matrices are equal. This may be explained by the fact that carbon, being a major element in the organic matrices and therefore does not present difficulties to atomise in enough quantity during ablative vaporisation, is readily abundant for excitation; with the additional observation that only the intensity of the ionic lines – whose emission in the discharge plasma normally precedes in time the detection of the neutrals – depends on the excitation efficiency enabled by halide volatilisation. The earliest atoms available in the discharge plasma are volatised atomic species with energies above ground state, so most of the energy extracted from the discharge plasma by these atoms is utilised more in the excitation of the atoms to ionic states than in the further liberation of atoms from the base matrix. The highest fraction of particles in the discharge however is that of atoms whose atomisation and excitation does not depend directly on the halide-enabled volatilisation. In this case, upon their ablative vaporisation energy must be extracted from the discharge plasma to atomise and excite them. Because these atoms have a higher population in the discharge, when that happens, the excess energy is hardly adequate to ensure any excitation process beyond neutral atom line excitation, i.e., few ionic species are excited. This is the case for the majority of the carbon atoms, which are readily available in the discharge plasma of the test organic matrices studied. That explains the differences in the radiation intensities observed between the neutral and ionic lines of the carbon lines.

The results of Fig. 5.8 are however based on observations of the line intensities of a major element and are therefore inconclusive with regard to the ability of the sliding spark technique to excite measurable spectral signals from trace elements embedded in the analysed matrices.

In Fig. 5.9, the ability of the sliding spark technique to measure the heavy elements in a typical analysis of a simulate ceramic powder under the conditions of halide matrix modifier is demonstrated using a mixture of 99.999 % pure Al_2O_3 and ZrO_2 powers. For a direct comparison the ceramic powder was bound in two matrices - borax and PVC - in the ratio of 1:1 for each matrix. In the analysis, one of the lines of boron, B II 345.228, was observed.

Unlike in the study reported in Fig. 5.8, it can be noted that, a host of Zr and Al lines are excited to measurable intensities. There are more Zr lines than Al lines observed, which well corresponds to the relative abundance of the respective elemental spectral lines excitable in the spectral window highlighted, as documented in the literature [215] - all the 38 possible lines for zirconium and the 7 for aluminium have been identified (not all are shown). The excitation temperature reached thus in the sliding spark is adequate to not only vaporise the ZrO₂ (Bp: 4500 ° C) and Al₂O₃ (Bp: 2980 ° C), it is also adequate to excite Zr II lines whose excitation energy is a high 13.13 eV.

For all the Zr and Al lines identified in the spectral window highlighted, the excitation efficiency of the elements in the simulate ceramic sample is higher as expected for both the background and line radiation, in the PVC than in the borax matrix. By comparing the measured and the relative intensities of the spectral lines documented in the literature [215] it may be observed that the halogen matrix influence is more pronounced for the less sensitive lines - such as Zr I 356.610, Zr II 355.195, Zr II 352.998, Zr II 351.048, and Zr II 346.302; and Al I 348.263, Al I 345.822, and Al I 344.487 - than for the more sensitive spectral lines.

The sensitive lines of Zr in the highlighted spectral region include Zr II 357.247, Zr II 355.660 and Zr I 354.768. This implies that the sliding spark technique, utilising halide volatilisation to modify matrix excitation, is more suitable for application in improving the atomisation efficiency of those elements which occur in the underlying matrix at trace concentrations than those that occur at major element concentrations. The results observed for the carbon line intensities, discussed earlier, in the various carbon-based matrices, validate this inference.

A possible explanation for this observation of the more enhanced trace element line intensities, is that the intensities essentially result from lines, which are not [yet] subject to self-absorption, i.e., trace element spectral lines in the sliding spark appear to emanate from an optically thin plasma.



Fig. 5.9 Characteristic spectrum showing elemental atomisation efficiency dependence on binding/modifier matrix for a simulate Al₂O₃-ZrO₂ ceramic powder bound in borax and PVC and excited by the sliding spark in air at atmospheric pressure

This provides the possibility to achieve representative calibration for the quantitative analysis of trace elements based on the halogen-assisted excitation mechanism in the sliding spark. As a result however, this observation, is not totally conclusive since the measured line intensities of the major elements may already be saturated due to self-absorption, in which case a direct comparison with the intensities of the trace elements which 'see' a thin plasma, is non-judicious.

In order to ascertain the analytical feasibility of the sliding spark technique utilising halide volatilisation for trace analysis, selected oxides from those shown in Table 5.2 were spiked in PVC to give spectral responses for the heavy metal in the range 0–2400 ppm.

Selected oxides were simultaneously spiked in the matrix in order to closely match typical samples, i.e., in practical environmental matrices a particular trace element hardly exists in isolation, so it is important that the respective elemental spectral responses in the sliding spark discharge plasma be examined in the presence of a complex matrix embedding several other elements in order to simulate a truer picture of the spectral interference and other multi-elemental effects in the matrix.

An example of such a scheme, providing data for the elements Co, Zn, Cd, Cr at various analyte concentrations but which all add to ≤ 2400 ppm in order to maintain constant elemental loading for a possible control on baseline (background) in each PVC pellet, is shown in Table 5.3.

Fig. 5.10 shows the results of intensity measurements for the elements at 300 ppm. Spectral responses in both polyvinyl-chloride (PVC) and polyvinyl alcohol powder matrix were examined. (In the latter the -Cl halide is replaced by the -OH functional group while the parent polymer chain remains the same).

The results confirm that the improved signal response in the halide matrices during the heavy trace element excitation in sliding spark technique is not due to the carbon matrix, but to the enhanced excitation of the ablated atoms as enabled by volatilisation through the halogenation process.

Table 5.3.Example of a sampling scheme which balances trace element loading levels and
baseline influence on the spectral response in the analysis of a PVC matrix
modifier for the excitation of the embedded elements in the range ≤ 2400 ppm

Spiked element concentration (ppm)										
Sample #	Zn	Cd	Co	Cr	Total					
1	300	1600	300	200	2400					
2	100	100	300	1900	2400					
3	200	1900	200	100	2400					
4	1050	200	100	1050	2400					
5	900	300	900	300	2400					

The peculiar result obtained for the Co I 340.512 is due to interference from the Cr II 340.330 and the Cd I 340.365 lines. Cd and Cr were simultaneously spiked with the Co in the PVC matrix – due to spectrometer drift and the peak identification algorithm used, it is difficult to isolate the Co I 340.512 line within the limits of the spectrometer resolution.

The difficulty of obtaining measurable trace analyte intensities in sliding spark spectrometry under unmodified matrix conditions is discernible from the results of Cd reported in Fig. 5.10. Cd is a volatile element, yet its inherent volatility is inadequate to ensure prompt excitation in the sliding spark discharge; halogenation is still necessary to enhance its detection. In sliding spark spectrometry thus, both volatility and ionisation (matrix-modulated) are important.

The use of halogenation techniques to enhance trace element excitation in sliding spark spectrometry should be even more suitable for the sediment matrix and other geological materials. This is because during the sliding spark vaporisation, halogenation can reduce complex matrix effects expected in sediment analysis; halogenation will not only increase the volatility of the analytes, it will accelerate the disintegration of the silicate structure. Most elements in a carbon-based matrix are easily chlorinated, and the chlorides have a high vapour pressure in the temperature range of the molten matrix in between the successive sliding spark discharges.

Exploitation of halogenation during sample evaporation was first carried out by Nickel and coworkers by addition of solid halides [216]. The analytical performance was improved for halogens in ETV by gas phase additives [217].

Based on these authors' experience, the halogenation process may be described by systematic thermodynamic calculations in the form of trend analysis [218,219]. The calculations, which however only describe the theory and experimental results of halogenation in ETV analysis, were based on the assumption of a closed system and normal pressure.

The aim was to describe, control, and improve the chemical reactions of sample evaporation by freon in graphite tube. Systematic calculations with all known gaseous chlorides, fluorides and oxides and their interactions were carried out for temperatures from 300 K.

The mathematical formulation of the problem for the general chemical system, which encompasses the sliding spark discharge, is very complex.

Reisch *et al.* [220] have also demonstrated the promotion of evaporation of Fe and Cd in a graphite matrix in direct insertion ICP analysis using $(C_2F_4)_n$ + NaF as a thermochemical additive. It was concluded that for the case of the highly volatile element Cd for which vaporisation begins at 800 ° C the $(C_2F_4)_n$ + NaF additive had a negligible influence on the volatilisation rate.

This result is not the same for the case of sliding spark spectrometry, probably because of the reasons already discussed with respect to the excitation of carbon matrix. The volatility of an element is modified by the compound form in which it exists in the embedding matrix.

Other reasons may have to do with the discharge optimisation. In the analysis reported in this dissertation, general conditions were used uniformly for the excitation of all the elements, where an equal number of scans were integrated to obtain the line intensities regardless of their temporal radiative characteristics in the discharge.



Fig. 5.10 Demonstration of halogen-enhanced trace element excitation efficiency in a typical nonconductor polymeric powder matrix excited by the sliding spark technique in air

From the work of the above-mentioned authors it was concluded that most alkalis are vaporised via the chlorides, and elemental form, and to some extent, via the oxides. The heavy metals are vaporised via oxides, chlorides and elemental form.

At high temperatures, vaporisation of oxides for a metal M includes three-following reactions [198]:

For oxides:

 $[MOx]_{s} \leftrightarrow (MOx)_{g}$ $[MOx] \leftrightarrow (MOx - \Delta x) + \Delta x/2 O_{2}$ $[MOx] \leftrightarrow [MOx - \Delta x] + \Delta x/2 O_{2}$ For chlorides: $[MCly] \leftrightarrow (MCly)$ $[MCly] \leftrightarrow (MCly - \Delta y) + \Delta y/2 Cl_{2}$ $[MCly] \leftrightarrow [MCly - \Delta y] + \Delta y/2 Cl_{2}$ (5.3)

Where the symbol [] signifies the condensed phase, while () signifies the gas phase.

5.8 Spectral Measurement

For all the measurements reported in this chapter, 90 spark shots were fired on the sample. This was done in order to compensate for pulse-to-pulse instability. In order to improve on the reproducibility and measurement precision (normally indicated by the RSD), intensities were acquired after analysing both sides of the pellets in triplicate; because of the instability of the sliding spark discharge, spectral intensity is best measured in terms of total integrated pulses.

Acquisition consisted of 9 independent measurements each integrating together 10 discharges of 330 ms spark pulse duration to evaluate the intensity. Reliable sparking was generally obtained at room temperature (\leq 35 ° C) and humidity range 10 % \leq 90 %, but occasionally the spark unit would experience spectral line drifts due to electronic overheating, or at low element

concentrations in the samples where there is greater uncertainty in the peak identification software.

The net intensities of the measured spectral lines were determined by baseline subtraction (2-point) method; here the intensity of the background is determined at two defined points left and right next to the particular measuring line peak maxima using a straight line equation and interpolated on the measured line. For these measurements, peak height was preferred to peak area.

5.9 System Reliability for Trace Quantitative Analysis

For reliable trace quantitative analysis to be accomplished by use of any technique, a comprehensive study of the technique's reproducibility and precision in the measuring of the intensity of photons excited from a typical analytical matrix is necessary. The precision, accuracy and repeatability of the analytical method ought to be examined. In this work, four replicates of intensity measurements were made utilising PVC matrix pellets prepared independently using the same sample preparation procedure.

The trace elements to be investigated were spiked as oxides with equal concentration in accordance with the scheme in Table 5.3. The result of the study, for arbitrarily selected elemental spectral lines from among those excited and measured, are shown in Fig. 5.11.

The relative standard deviation of the measured intensities from a typical heavy element embedded in the PVC matrix at three concentration levels up to 800 ppm are shown in Fig. 5.11. It may be noted that the values lie between 6 - 15 %, with the poorest being generally about 15 %, as expected, of blank samples. Theoretically, near the detection limits this figure of merit is generally low but it should, for a reliable quantitative analytical technique, improve as the quantity of trace element concentration in the matrix increases.

The results indicate that the intensities of trace elements at the level of 100 ppm, in a typical solid sediment matrix may reliably be excited and measured with satisfactory relative standard deviation of about 10 % - lower if the more sensitive lines, which are more suitable for selection for use in quantitative analysis, are measured and when the instrumentation of the sliding spark technique is optimised for improved spectral excitation.



Fig. 5.11 Estimation of the typical precision (a) in replicate intensity measurements in the sliding spark, defined by mean RSD values in comparison to (b) the repeatability of the replicate intensity measurements against the 100 % standard

Reproducibility of the measured intensity was also investigated by measuring the intensities of selected lines among sample replicates. Except, again, for the blank, whose intensity repeatability fluctuates widely (87 % - 95 %), the rest of the concentration levels whose intensities were measured show satisfactory stability of near 100 % with a \pm 3 % fluctuation; this analytical figure of merit improves with element concentration due to the better signal to noise ratio obtainable for the higher element concentrations in the analysed matrix.

But far the most critical characteristic to investigate for the potential of any spectrometry technique to perform trace element analysis is robustness. To study the temporal stability of the sliding spark technique and reproducibility of the system in terms of measuring the intensity of photons excited from trace elements, samples were prepared with element concentrations of 500 ppm embedded in a PVC matrix.



Fig. 5.12 Evaluation of the sliding spark temporal reproducibility (a-c) for various spectral lines emitted by elements spiked at trace level in PVC and (d-f) the spectrometer performance characteristics over a quarter year period with respect to both temporal reproducibility and precision in the intensity measurements

The intensity measurements for randomly selected spectral lines of Ti, C, and V were made every week over an interval of twelve weeks, in which the spectrometer remained powered. Replicate sample pellets, which had been prepared in one procedure, were utilised in the measurements. The results are shown in Fig. 5.12; the reproducibility of the sliding spark technique with respect to trace element analysis over the 12-week interval (Fig. 5.12a-c) is satisfactory. The excellent results reported for the mean relative standard deviation for the intensities of the C I 247.856 line, relative to the other lines, is due to the fact that carbon is a major element of the PVC matrix, as opposed to Ti and V, which were spiked.

Besides the relative abundance of carbon, which is high enough to guarantee small RSD vales in the intensity measurements, this also suggests that the homogeneity of the prepared samples plays a critical role in the precision of the intensity measurements.

No intensity variations could be attributed to the fact that the spectral lines either emanate from neutral or ionic species. The mean RSD for the intensities reported (Fig. 5.12 d, e, f) lie at about a mean value of 10 % for the studied elemental lines, with a standard deviation - over the period of 12 weeks - of less than 3 %. Similarly, these analytical figures of merit are expected to drop to below 10 % for those lines that are finally selected for quantitative analysis, and when the technique is optimised for improved spectral excitation.

6.0 The Characteristics of Sliding Spark Spectra

6.1 Introduction

It was ascertained in Chapter V that for a sliding spark discharge plasma excitation of the heavy elements in a non-conductive solid matrix is significantly increased in the presence of halogens as compared to a non-halogen containing matrix, through the formation of volatile halides. It can be postulated therefore that, sensitive detection of spectral lines of quantitative analytical utility may be achieved in a permanent manner in sediment matrices in the presence of a halide matrix modifier; that would be an essential step towards obtaining comprehensive quantitative results in applied analysis at trace level, from sliding spark spectrometry.

This chapter reports the results of spectroscopic measurements of discharge plasma produced by atomisation and ionisation by sliding sparks in air at atmospheric pressure of the surface layers of non-conductor materials in a study that aimed to evaluate the sliding spark discharge technique as a radiation source for *in situ* solid-state trace quantitative spectrometric analysis. The motivation of the study was to develop an effective methodology for both analyte line selection and for the management of spectral line overlaps during typical trace element analysis of matrices having complex composition.

The optical spectra emitted by analyte species excited in dense discharge plasmas have recently become the subject of extensive study. The motivation of these studies, is apparently, to develop effective methods for both analyte line selection and for the management of spectral line overlaps during multi-elemental analysis of having high matrix samples, such as may be encountered in laser-induced breakdown spectroscopy in air, or in surface sparks at high pressures. In the present study, results of the following investigations are presented:

- The characteristics, with respect to trace quantitative analysis, of sliding spark-excited spectra of typical non-conductor modifier matrices in air at atmospheric pressure. For a spectroscopic interpretation of the excited spectra to be useful, comparison was made between inductive and non-inductive discharges in order to infer how they relate to the spectral line intensities detected from trace elements spiked in the matrices as oxides.
- The capability of the sliding spark source to excite intense interference-free emission line spectra suitable for direct trace spectrochemical analysis of solid non-conductor matrices.

- The identity and nature of the spectral lines excited, in particular if they have algorithmic response functions in the trace level concentration regime. The study concentrated on the search for intense, optically thin lines, and their quantitative analytical figures of merit.
- The possibility to measure and utilise multiple spectral lines in correlating the emission spectral features with the sample matrix chemistry. This would be a prerequisite to the use of multivariate calibration in chemometrics in order to increase both the reliability of trace quantitative evaluation and the possibility to effectively monitor the baseline/ background for changes in excitation (which can provide insight into the physical mechanisms involved in excitation) in quantitative analyses [221-223] where there is difficulty of finding wavelength regions in which the sensitive analyte lines are undisturbed [224].

6.2 Emission Spectra Excited from a PVC Base Matrix

In the early studies of vacuum sparks for far UV spectroscopy which were initiated by Vodoar and Astoin in 1950 [28] the intense UV radiation that was obtained when organic polymers were used as substrates was attributed to the rich carbon spectra [225]. Small concentrations of organic molecules can significantly alter the emission characteristics of the surface discharges, even when the predominant molecules are air gases.

In the case of sliding spark excitation performed in air at atmospheric pressure in a PVC matrix spiked with heavy trace elements in their oxide form (see Chapter V for the sample preparation procedure), a rich analyte signal yield is discerned in a composite radiation spectrum of the resulting discharge plasma, superimposed on a complex and high background which fluctuates with a magnitude that is dependent on both the wavelength region and on the polymer matrix composition (Fig. 6.1a & Fig. 6.1b). For the range of T_{e} encountered in a typical sliding spark discharge plasma, a significant fraction of the total emission is due to recombination continua, especially for $\lambda < 400$ nm. The prospects of analysing trace elements in non-conducting solids to good detection limits using the sliding spark is thus to a large extent undermined by the high level of the continuum background emitted by the discharge and by its fluctuation; such a background in plasma emissions is known to be mostly due to the recombination of electrons with positive ions or to occur because of the retarding effect of the electron movement in the electric field of the ions [226,227].

The spectral background exhibits a general rise, which is then followed by a drop in the intensity of the continuum with increasing wavelength from the UV to the visible. The spectral characteristic of this emission is that it is continuous and therefore overlaps most of the analysis lines, particularly under hard discharge (Fig. 6.1b). The high number of line overlaps in both spectra (Fig. 6.1a & Fig. 6.1b) is due to the high density of the charged particles and their high

collision frequency in the sliding spark discharge plasma channel, which leads to complex pressure and Stark broadening [228]. Very few spectral lines are free from spectral interference - both from the ambient plasma species, cathode material emission, and also from the major components of the underlying matrix including their reaction products. This spectral interference also undermines the prospects for utilising some of the well-known spectral emission lines of high intensity in trace quantitative spectrometry using the sliding spark operating in air at atmospheric pressure. When quantitative analysis is intended, spectral line overlaps from atomic, ionic and molecular contaminants can degenerate the accuracy of the results and considerably worsen the analyte detection limits.

Introducing into the spark circuit an air induction coil provides the possibility to change the characteristics of the discharge, and therefore the spectra. For weak discharges corresponding to $V_C/L \le 10^8 \text{ V/H}$, a weak continuum and a few lines of exited air species, substrate and electrode species are observed. The characteristics of the discharge are said to be 'soft', and the emission spectrum has fewer, mostly atomic lines (Fig. 6.1a); i.e., the spectra are arc-like – in arcs, it is believed there is a lower degree of ionisation because ionisation energies are even higher than excitation energies. Self-absorption and line reversal are thus more critical.

Lapermiental details	for the generation of the test speetra
Capacitance	14 µF
Discharge condition	'Hard'/ 'Soft'
Scan time	500 ms
Scans	10 (plus 1 extra pre-spark)
Electrode gap	4.5 mm

 Table 6.1
 Experimental details for the generation of the test spectra

The spectra exhibit a more complex structure under 'hard' discharge (non-inductive discharge) conditions. The spectra are composed of more lines, which include transitions from ionic states. As the discharge strength is increased, more lines transitions are excited and become increasingly broad as a result of Stark effect. The line centres of most elements become optically dense so that stronger (harder) discharges are characterised by appreciable line broadening and a more prominent continuum component.

The discharge hardness essentially imposes the upper limit for the initial rate of change of the discharge current, a quantity that determines the rate of energy input into the discharge channel (see Fig. 4.3). Where the spectral lines are not highly broadened, as for instance in the UV region the lines are easily identifiable against a weak continuum (Fig. 6.1b).



Fig. 6.1a Typical sliding spark spectra of different matrices excited under 'soft' discharge for each of the three CCD detectors used to measure the radiation



Fig. 6.1b Typical sliding spark spectra of different matrices excited under 'hard' discharge for each of the three CCD detectors used to measure the radiation

Some broad bands appear in both spectra (Fig. 6.1a & Fig. 6.1b) which can be attributed to the organic matrix and well-known molecular transitions from species like H, N and C; the most prominent one occurs around 385 nm due to the CN B - X transition. (In dense plasmas at high densities $> 10^{19}$ cm⁻³ the spectral lines from low ionisation stages are normally very broad).

The spectral widths of the vibrational lines are related to the rotational temperature of the excited free molecules in the matrix and air. Emission of CN radicals is dominant throughout the spectrum. The CN in particular is a nascent species in the discharge plasma. In a variety of electrical, microwave, or RF-induced discharges, multiple CN emission bands arise in the presence of carbon and nitrogen compounds.

Abundant CN bands, corresponding to the violet system (see Fig. 6.2) and other systems, occur throughout the ultraviolet region of the spectrum and either coincide directly or are immediately adjacent to many of the most sensitive emission lines of the heavy elements to be measured. CN emission bands are abundant in the spectral region between 170 and 420 nm. The most prominently visible CN emission occurs around 421.600 nm corresponding to the $0\rightarrow1$ transition of the CN B² Σ — X² Σ violet system.

There is also a violet system CN band at 388.34 nm, and another one at 359.255 nm. For many heavy metals, the relatively broad CN emission bands overlap the atomic peak positions that may even be selected for background measurements [229]. The CN bands are formed in the periphery of the carbon vapour plume principally through the reaction:

$$C_2 + N_2 \Leftrightarrow 2CN$$
 (6.1)

The spectra are not just made up of the net analyte signals emanating from the elemental species; a composite radiation (line plus background) appears in most spectral windows centred on an analysis line (e.g., the H_{α} 486.133 line in Fig. 6.2).

A large number of chlorine and carbon lines, including lines arising from singly and doubly ionised species are observed. Every excited matrix constituent atom and molecule features specific spectral signatures: the spectral lines emitted by free atoms or ions, or the molecules of the excited elements embedded in the excited matrix and the interference background, all which are simultaneously detected.





The background consists of a continuous intense radiation (mostly from the visible regime: from ≈ 340 nm) initially emitted from the matrix and air, radiation from the discharge environment and electrodes, radiation scattered in the spectrometer, and radiation from molecular bands originating from the reaction products of the air in the electrode gap plasma with the matrix components. NH, OH C₂, CO bands have also been observed (Fig. 6.2). Diatomic molecular oxygen bands also appear owing to the presence of significant ambient amounts of oxygen nitrogen and moisture in the atmosphere. They are all caused by excited matrix species ablated from the sample, and by impurities the plasma matrix. A considerable amount of adsorbed grains of water released into the discharge also reduces the yield of the ionisation of the matrix atoms in the plasma. In addition, it strongly affects the reproducibility and sensitivity of the analysis [230-233].

A better observation and explanation of the band systems is possible if a time-evolution of the continuum emission is recorded by a gated CCD system.

λ (nm)	Molecule	System	Transition
487.30	H_2	Hydrogen	
486.13	$H_{m eta}$	Hydrogen	
485.66	H_2	Hydrogen	
485.65	СН	4300 Å	$A^2\Delta - X^2\Pi$
433.66	OH	Schüler-Woeldike.	$B^2\Sigma^+ - A^2\Sigma^+$
425.22	CN	Le Blanc's	$B^2 \Sigma - A\Pi$
424.89	CO^+	Commet-tail	$A^2\Pi - X^2\Sigma$
422.53	CH^+	D-H	$A^{1}\Pi - X^{1}\Sigma$
402.78	NO	ß-system	$B^2\Pi - X^2\Pi$
388.34	CN	Violet	$B^{2}\Sigma - X^{2}\Sigma$
387.14	CN	Violet	$B^{2}\Sigma - X^{2}\Sigma$
387.13	СН	3900 Å	$B^2\Sigma - X^2\Pi$
386.19	CN	Violet	$B^{2}\Sigma - X^{2}\Sigma$
385.79	N_2	2 ⁺ system	$C^3 \Pi_u - B^3 \Pi_g$
385.22	C_2	Desld'A.	$C^1\Pi_g$ — $B^1\Pi_u$
385.09	CN	Violet	$B^2\Pi - X^2\Sigma$
359.04	CN	Violet	$B^2\Pi - X^2\Sigma$
350.30	CH^+	Violet	$B^{1}\Delta - A^{1}\Pi$
288.52	NO-ß	ß-system	$B^2\Pi - X^2\Pi$
288.50	\mathbf{NH}^+	2885 Å	$C^2\Sigma - X^2\Pi$

Table 6.2Major band systems excited in hard sliding spark discharge in a typical matrix

These spectral characteristics imply that in applications of sliding spark spectrometry analysing trace elements, the use of controlled atmospheres may be necessary to eliminate the CN and other bands detected, which obscure the sensitive lines of the elements, in order to enhance the sensitivity of elements to obtain spectral responses with respect to the background. But the atmosphere employed must be transparent to the many short UV wavelengths observed, which are necessary for applied quantitative spectrometry. The atmosphere employed also affects the background generally. Nonetheless, air is preferred for instrumentation simplicity.

6.3 Spectral Line Identification and Measurement

Trace analysis of samples, which emit line–rich spectra continues to be a major challenge in all plasma-source spectroscopy. The amount of spectral data collected during a typical discharge is in general huge; because of the necessity to ensure good temporal resolution, the need to utilise multiple channels on the one hand, and the integration of long discharges of the individual sparks (25–1000 ms) on the other.

A basic problem in sliding spark spectrometry is the isolation of a net analyte signal from the complex spectrum. Spectral interference, which can lead to incomplete isolation of the net signal at the analysis line, seriously affects the accuracy of analysis, particularly when high concentrations of matrix are present.

Observations of the emitted radiation over a broad wavelength range (212-511 nm) allow simultaneous measurements of the analyte lines emitted from the excited materials. In this spectral region there is a continuum with the analyte line spectrum superimposed upon it. The spectral lines have Voigt profiles due to the convolution of the Lorenzian and the Gaussian profiles caused by the Doppler, Stark and instrumental broadening. It is clear sliding spark spectra are considerably more complex compared to DC-arc spectra. Because line transitions originating within the emitting discharge volume are highly Stark-broadened, absorption of radiation passing through the cooler zones must of necessity occur at the line centres.

In the work reported in this dissertation a total of 318 lines were detected, measured and systematically identified for the 14 elements that were studied. A spectral compendium of the lines is given in Tables 6.3a - d. The samples were prepared as reported in Chapter V. The samples were analysed according to the scheme shown in Table 6.1. Each spectrum was scanned for three signals – the blank, air and analyte element spiked at 500 ppm - and the lines identified according to the procedure discussed in section 6.5. The lines listed in Tables 6.3a - 6.3d were obtained for element oxides spiked in PVC. It may be assumed that the same lines are excited in

a typical non-conductor sample bound in a PVC matrix by sliding spark operating in air at atmospheric pressure under modest opto-electronic excitation parameters.

It suffices to note that the various oxides of some of the elements analysed exhibit different spectral characteristics that depend on the oxidation state of the oxide in the matrix. The tabulated results also suggest that this characteristic can be modulated to an extent by the discharge strength. The elements that exhibit this spectral characteristic (depending on the oxidation state) for several lines are: Co, Fe, Ti, V, Cr, Mn and Pb.

This is an important spectral property if sliding spark spectrometry is to be useful for a comprehensive analysis of complex environmental matrices such as sediment. Most studies dealing with heavy metals in natural systems (e.g., metals associated with suspended matter or bottom sediments) concern total metal concentration. Use of total concentration as a criterion to asses the potential effects of trace element contamination implies that all forms of a metal have equal impact on the environment, an assumption that is clearly untenable. Relatively few attempts have been made to evaluate the speciation of the metals.

The species-sensitive spectral line intensities in the work presented in this dissertation present a promising alternative on this front if the species-sensitive lines measured possess the analytical figures of merit that could make them to be selected as candidates for calibration for quantitative analysis.

Cu				Ni			Со					Zn			
Cu 2+	[0]	Cu 1+[0]]	Ni 3+[O]	Ni	2+[CO ₃]		Co 3+[O]		Co 2+[S]			Zn 2+[O]		
Hard	Soft	Hard	Soft	Hard	Soft	Hard	Soft	ft Hard		Soft	Hard	Soft	Hard	Soft	
I 327.396 I 324.754 II 236.989 II 224.700 II 224.261 I 222.778 II 221.810 II 221.026 II 219.226 II 217.940 II 213.436	I 327.396 I 324.754	I 327.396 I 324.754 II 236.989 II 224.261 II 221.810 II 221.026 II 217.940 II 213.598	I 327.396 I 324.754	I 361.939 I 356.637 I 352.454 I 351.505 I 351.034 I 349.296 I 347.255 I 346.165 I 345.847 I 344.626 I 341.394 I 339.299 I 338.057 I 310.771 I 306.462 I 305.432 I 301.914 II 243.789 II 241.614 I 231.603 II 220.298 II 227.021 II 227.021 II 226.446 II 221.647	I 361.939 I 352.454 I 351.034 I 341.394	I 361.939 I 356.367 I 352.454 I 351.505 I 351.034 I 349.296 I 347.255 I 346.165 I 345.847 I 344.626 I 341.394 I 339.299 I 338.057 I 310.771 I 306.462 I 305.432 I 301.914 II 243.789 II 241.614 II 223.603 II 227.877 II 227.021 II 226.446 II 221.647		I 389.408 I 387.312 I 358.719 I 356.983 I 352.981 I 352.685 I 352.343 I 352.157 I 351.835 I 351.264 I 350.984 I 350.632 I 350.228 I 349.569 I 348.940 I 347.402 I 347.270 I 346.580 I 345.351 I 344.917 I 344.364	I 343.304 I 341.234 I 340.512 I 339.538 II 338.817 II 258.722 II 258.224 I 258.084 II 256.404 II 255.941 II 252.987 II 240.875 II 238.345 II 237.862 II 236.379 II 231.498 II 231.160 II 230.786 II 228.616	I 389.493 I 356.983 I 352.343 I 352.157 I 351.835 I 350.984 I 350.228 I 347.402 I 346.580 I 345.351 I 344.917 I 344.364 I 341.234 I 340.512	I 389.408 I 387.312 I 358.719 I 356.983 I 352.981 I 352.981 I 352.685 I 352.343 I 351.835 I 351.264 I 350.632 I 350.228 I 349.569 I 348.940 I 347.270 I 346.580 I 345.351 I 344.917 I 344.364 I 343.304 I 341.234 I 340.512 II 258.722 II 258.224 II 258.722 II 258.224 II 258.722 II 258.722 II 258.224 II 258.722 II 258.725 II 238.892 II 235.343 II 230.786 II 230.786 II 228.616	I 345.351	I 472.216 I 468.014 I 334.502 I 330.259 II 226.600 II 255.796 I 213.856	I 472.216 I 334.502 I 330.259 I 213.856	

Table 6.3aSpectral lines excited from elements embedded in a PVC polymer matrix and measured in air at atmospheric pressure by use of sliding spark
spectroscopy for elements (concentration: 500 ppm) spiked in the matrix as oxidesⁱ

ⁱUunless indicated otherwise.

Hg Hg 2+[O] Hg 1+[C]] Fe			3+[O]	Fe	Fe 2+[O	ו	Ti Ti 4+[O] Ti 2+[O]					Al Al 3+[O]		
Hard	Soft	Hard	Soft	Hard	Soft	Hard	Soft	Hard		Soft	Hard	Soft	Hard	Soft
II 398.396 I 366.288 I 365.015 II 319.103 I 280.443	1365.015			I 382.588 I 382.043 I 381.584 I 376.376 I 375.823 I 374.556 I 373.487 I 371.994 I 364.785 I 363.147 I 361.876 I 358.119 I 357.010 I 302.564 II 276.893 I 275.786 I 275.014 I 276.893 I 275.786 I 275.014 I 276.111 II 261.187 I 259.940 II 258.588 II 256.347 II 255.002 II 253.850 II 241.107 II 240.488 II 239.562 II 238.207 II 234.349	I 375.823 I 371.994 I 364.785 I 363.147 I 358.119 I 357.010			I 499.107 I 498.173 I 457.090 I 399.864 I 398.976 I 395.821 II 391.346 II 390.054 II 375.929 I 375.286 I 374.106 II 368.519 II 365.224 II 365.976 I 365.350 II 364.133 II 362.483 II 353.541 II 352.025 II 351.084 II 350.489 II 349.105 II 347.718 II 346.150 I 345.638 II 345.247 II 344.431 II 339.457	II 338.783 II 338.776 I 337.279 II 336.121 II 334.903 II 334.903 II 334.188 II 333.520 II 332.158 II 328.766 II 327.677 II 326.025 II 322.801 II 324.860 II 323.966 I 323.822 II 323.452 II 323.455 II 323.457 II 307.855 II 307.297 II 306.328	I 498.173 I 399.864 I 398.976 I 395.821 II 376.132 II 375.929 I 365.350 II 338.783	II 376.132 II 375.929 II 368.519 II 338.783 II 338.376 II 337.279 II 336.121 II 334.903 I 317.092	II 376.132 II 375.929 II 338.783	I 396.152 I 394.401 II 365.500 I 220.462	I 394.401

Table 6.3bSpectral lines excited from elements embedded in a PVC polymer matrix and measured in air at atmospheric pressure by use of sliding spark
spectroscopy for elements (concentration: 500 ppm) spiked in the matrix as oxides^j

^j Unless indicated otherwise
V 5+[O] Hard Soft	V V 4+[Hard	O] Soft	V3+[Hard	Cl] Soft	Cr Cr 6+ Hard	-[O] Soft	Cr 4+[O] Hard		Soft	Hard	Cr 3+[C Soft	^{D]} Mn 4 Hard	Mn +[O] Soft	Mn 3 Hard	+[O] Soft	N Hard	In 2+[CO ₃] Soft
II 400.571 II 374.581 II 373.276 II 371.548 II 375.680 I 355.680 I 355.680 I 355.680 I 354.519 II 355.680 I 354.43 II 350.443 II 327.112 II 326.589 I 319.985 II 319.757 II 315.132 II 314.682 II 313.333 II 313.026 II 312.528 II 311.838 II 310.937 II 310.941 I 306.965 I 306.046 II 305.594 II 305.589 II 305.589 II 305.589 II 305.589 II 305.589 II 305.589 II 305.589 II 305.589 II 305.589 II 305.594 II 305.589 II 305.589 II 305.589 II 305.589 II 305.589 II 305.589 II 305.589 II 305.594 II 305.589 II 305.589 II 305.594 II 305.589 II 305.580 II	I 355.680 I 354.519 I 319.985 II 319.757 II 313.333 II 312.528 II 311.838 II 310.937 II 303.976 II 289.560		II 373.602 II 313.333 II 312.528 II 311.838 II 310.937 II 310.094 I 306.965 II 303.976 I 292.764		I 359.431 I 357.868 II 336.804 II 313.205 II 312.869 II 305.953 I 297.548 I 284.602 II 267.879		I 396.369 II 371.128 II 367.767 II 363.149 I 360.532 I 359.348 II 358.530 I 357.868 II 345.084 II 340.876 II 340.876 II 340.330 II 338.268 II 337.939 II 336.804 II 336.804 II 336.804 II 338.5516 I 318.983 I 315.516 I 314.439 II 313.668 II 312.805 II 312.805 II 312.502 II 308.788	II 305.547 II 304.745 II 303.294 II 302.664 I 302.067 I 299.406 II 298.918 I 298.401 I 297.548 II 297.548 II 287.845 II 287.845 II 287.845 II 287.845 II 287.845 II 286.510 II 286.510 II 286.512 II 284.602 II 282.453 I 284.602 II 282.453 I 284.602 II 282.453 I 281.794 I 281.75.185 II 269.934 II 267.283	I 360.532 I 359.348 I 357.869 II 336.804 II 313.205 II 312.869 II 287.845 II 287.043 II 284.983 I 284.602	II 345.084 II 313.205		I 482.352 I 405.554 I 403.076 I 382.351 I 356.949 I 354.803 I 353.212 II 349.754 II 349.754 II 349.754 II 348.291 II 347.413 II 346.033 II 344.198 II 295.302 II 294.314 II 293.638 I 289.266 II 271.158 I 270.366 II 263.984 II 262.559 II 261.814 II 260.569 II 259.373 II 257.610 II 256.365	I 482.352 I 356.949 I 353.212 II 348.868	I 356.949 I 354.803 II 348.868 II 347.413 II 346.033 II 344.198 II 294.314 II 293.638 II 261.814		I 482.352 I 476.238 I 475.404 I 405.554 I 403.076 I 401.810 I 382.351 I 356.949 I 354.803 I 353.212 II 349.754 II 349.584 II 349.584 II 349.584 II 349.584 II 347.413 II 346.033 II 344.198 II 295.302 II 294.314 II 293.638 I 289.266 II 271.158 I 270.366 II 263.984 II 263.984 II 260.559 II 261.814 II 260.569 II 257.610 II 256.365	1 403.076

Table 6.3cSpectral lines excited from elements embedded in a PVC polymer matrix and measured in air at atmospheric pressure by use of sliding sparkspectroscopy for elements (concentration: 500 ppm) spiked in the matrix as oxides^k

^k Unless indicated otherwise

Table 6.3dSpectral lines excited from elements embedded in a PVC polymer matrix and measured in air at atmospheric
pressure by use of sliding spark spectroscopy for elements (concentration: 500 ppm) spiked in the matrix as oxides¹

As						Cd			
As 5	As 5+[O] As		3+[O]	Pb 4+[O]		Pb 2+[O]		Cd 2+[O]	
Hard	Soft	Hard	Soft	Hard	Soft	Hard	Soft	Hard	Soft
		Ι	I 234.984	I 405.782	I 405.782	I 405.782		I 508.582	I 508.582
		234.984		I 368.347	I 368.347	I 368.347		I 479.991	I 479.991
				I 363.958	I 363.958	I 363.958		I 361.051	I 361.051
						I 308.909		I 346.765	I 346.620
								I 346.620	I 228.802
								I 340.365	II 226.502
								II 231.277	II 214.414
								I 228.802	
								II 226.502	
								II 214.414	

¹ Unless indicated otherwise

6.4 Sliding Spark Analyte Spectral Responses

In sliding spark spectrometry patterns of emission appear to evolve during trains of the sparking shots - the scan-by-scan patterns are different and appear to be functions of, among other factors, whether the measured line is from an ionic or neutral species, and the overall composition of the matrix.

All the spectral measurements were made according to the conditions reported in Table 6.1.

The analytical range of a significant number of the analyte spectral lines identified is characterised by short linear ranges. Most species lines exhibit sheared S-shaped spectral responses with only small linear portions in the low trace (typically \leq 1000 ppm) concentrations (see, e.g., Fig. 6.3). Severe absorption effects predominate soon after, due to the fact that the sliding spark discharge is a dense transient plasma, which expands and cools at frequencies sufficient to affect the absorption cross sections of the emitted lines. This results in a lack of good sensitivity linearity for most elemental lines excited.

It can also be concluded that the matrix effect variations, which become more pronounced for most elements at concentrations ≥ 1000 ppm, are not only a function of the discharge behaviour: as the concentration of the spiked elements increases the sample composition changes fundamentally so that the spectral response curves represent a convolution of complex processes rather than a simple functional response of intensity with respect to elemental concentration, leading to the perceived difference between the matrix influences on the signal obtained from different specific concentration regimes of the analyte.

As may be observed in Fig. 6.3 (and demonstrated in Fig. 6.4), the line intensities initially increase in direct proportion with increasing element concentration due to the increase in the emitting species ablated in the discharge plasma, then levels off as self-absorption effects begin to predominate; at higher concentrations, depending on the element and species spectral line, when the maximum of the absorption has been attained, the emission cross section again exceeds the absorption coefficient, and the discharge plasma resumes to exhibit spectral response in which the line intensity is nearly linearly correlated with the concentration of the emitting species. Examples of this are observed in Fig. 6.3 for Y II 354.901 and Fe I 382.043.

When the spectral responses in the low concentration region are examined (as opposed to the spectral responses at higher analyte concentration), both the spectral peak height and the peak areas seem to be directly proportional to the element concentration (see for instance Y and Al lines in Fig. 6.3, and the Ti and Mn peaks in Fig. 6.4). Quantitative analysis at trace level using the sliding spark is therefore feasible. Only a few lines are found to be available however for

calibration for possible quantitative analysis to varying extents of concentration range. These are the lines to which the sliding spark plasma is optically thin.

The effect of self-absorption is therefore significantly reduced by analysing the analyte lines at low trace concentration. This is what is desirable in direct solid analysis in spite of the possible complications that could result from noise and background; however, methodological and instrumental improvements are available which can address these problems.

It can be concluded that emission spectroscopy is only useful to detect atoms, ions, radicals or molecules present in the sliding spark a discharge plasma, if it concerns only the species that have concentrations quite low compared to their parent species in ground or metastable states.

6.5 Line Selection

The selection of a useful line for analysis in a given sample is a tedious one as most elements have many lines excited and available for analysis. It was decided in the work reported in this dissertation to select the wavelengths at which little or no interference was recorded, regardless of the sensitivity. Selection was performed using the oxides standards spiked in a PVC matrix sampling in the concentration interval 0 - 5000 ppm of each tested element.

In order to find the wavelength regions where sensitive analysis lines are undisturbed for use in accurate calibration, measurements were made for all the spectral lines detected. Each element was first investigated in a group. Mixtures, of up to three elements, were studied in order to measure the elements as close to their natural existence as possible, viz. in a typical matrix other elements exist simultaneously and line interference would be expected. The elements were then examined separately for comparison. This is because the atomisation and excitation cross section of each trace element depends uniquely on the discharge plasma-dependent characteristics of the matrix elements such as ionisation potential, cross section of electron impact, surface vapour pressure, and boiling point of the components in the matrix.

This was done starting with the examination of the linearity responses at low concentrations of the spiked elements then proceeding in increasing order, at short concentration intervals (since the spectral responses tend to fluctuate rapidly with respect to the analyte species concentration), up through minor, to the high and ultimately the percent concentration range – each time, especially in the minor concentration level regime, while decreasing the concentration interval in order to probe the spectral responses at a much more shorter concentration ranges to be able to determine more precisely the spectral response plateaux.



Fig. 6.3 Typical emission spectral response characteristics of the 'hard' sliding spark discharge

In the line selection procedure not only was the intensity, and intensity-concentration correlation (which must be algorithmic at low concentrations) considered, but also whether each line was free from spectral interference – both from the plasma and other matrix component lines. Additionally, the nature of the emission - atomic or ionic – was considered; it was observed that in principle elements undergoing transitions of ionic type tend to experience fewer consequences due to changes in the plasma operating conditions and are therefore potentially more suitable for analyses of complex matrices.

This is probably because these lines, having been emitted and radiated in the earlier stages of the discharge, are detected before the plasma expands outward at the speed of the shock wave front and cools, thereby absorbing any spectral lines emitted from the discharge plasma core pronounced self-absorption. There are three main contributions to radiative absorption: inverse bremsstrahlung (free-free) and absorption by molecular and atomic states (bound-bound) and (bound-free). Absorption in the visible region is negligible for air at room temperature but increases significantly at higher temperatures.

The change with time of the emission with respect to the degree of ionisation in pulsed discharges may in principle be observed in time-resolved spectra; ion lines appear most strongly early in the discharge cycle and neutral lines are weak or absent until later in time see Chapter IV). Neutral species in surface sparks peaks 10-30 μ s after the peak continuum intensity, and is observable for a time considerably in excess of the discharge duration, i.e., after the excitation current has fallen to zero. Ionised species reach peak intensity in a few μ s and radiate only during the period of appreciable current flow.

Theoretically, the wavelengths selected for analysis should have a large transition probability in order to reach high signal to noise ratios and better time resolutions particularly in time-resolved spectroscopy. However, line radiation from typical dense plasmas may require the selection of transitions with lower oscillator strengths. Depending spectral region considered and on the sensitivity range of the detector for the considered spectral region, even lines with weaker oscillator strengths were selected. But in order to decrease the influence of self-absorption on the measurement accuracy, only optically thin lines were selected. Nonetheless some of the well-known sensitive lines of the elements could not be selected for use in quantitative analysis owing to the possible interference of the spectral lines of major matrix components from air, electrode material, and the base matrix. Such lines include for example V I 439.000, Cr I 428.973, Cr I 427.481, Ti I 430.592, Fe I 438.355 and Fe 427.176.



Fig. 6.4 Line identification and selection for trace element spectral responses in a PVC matrix

6.6. Spectral Linearity Calibration Tests for Quantitative Analysis

Traditional search for a spectral response linearity that is suitable for quantitative analysis calibration is done by varying the analyte content while monitoring the instrumental response. A preliminary calibration for quantitative analysis may be based on the use of synthetic standards addition/linear additive model other than robust multivariate linear regression.

The application of an analysis technique to trace metrology problems is however to a large extent governed by the achievable analytical sensitivity for the species of interest in a given matrix. The sensitivity reflects the ability of the technique to discern a small change in the species concentration made to a distinct relative detection limit determined at specified (normally the 3 σ) degree of statistical confidence.

In order to successfully apply the sliding spark spectrometry to quantitative elemental analysis in materials characterisation where analysis at the trace level is critical, it is therefore imperative to understand, for each element of interest in the sample matrix, the minimum and maximum analyte concentration that can be analysed and with what spectral sensitivity that may be done. This is determined by that concentration, which gives a signal that is several times greater than the average fluctuation in the signal, extracted from the radiation detector due to the background and noise, and in addition, by a spectral response that is algorithmic over the trace concentration range examined.

A total of 50 spectral lines (Table 6.4) were selected for possible use in calibration for the quantitative analysis of 13 out of the 14 elements studied (no suitable line was identified for As). A comparison is made between these lines and the traditionally sensitive analytical lines in emission spectroscopy (summarised in Table 6.5); this is a good gauge the capability of the sliding spark spectrometry technique to perform analyses based on the traditionally sensitive emission lines. As can be observed, most of the spectral lines traditionally used in quantitative emission analysis (shaded in Table 6.4) are also excited in the sliding spark discharge plasma.

Some of the weaker lines are relatively close to certain strong lines, making their peak intensity difficult to determine because of the limited spectrometer resolution (0.05 nm). However, some of the sensitive lines that are excited are only qualitatively analytically useful. Selected examples of spectral responses for the elements measured in the PVC at increasing ppm concentration levels are shown in Fig. 6.5a & Fig. 6.5b. The responses, which have been obtained and fitted on the row data by linear regression without the use of error bars, demonstrates clearly the utility of sliding spark spectrometry in trace element analysis.



Fig. 6.5a Selected examples of the analytical performance curves for trace elements excited by the sliding spark in PVC



Fig. 6.5b Further selected examples of the analytical performance curves for trace elements excited by the sliding spark in PVC

To the best of the author's knowledge, the optically thin nature of some species lines in surface sparks, which are suitable for applied quantitative trace analytical spectroscopy has not been described before. This characteristic manifests itself in the broad range of linear relationships obtained between the analyte responses and the concentrations for the 13 elements analysed embedded in the PVC polymer in their oxide form. For the first time quantitative results at trace level from the direct analysis of solids by sliding spark spectroscopy are shown to be feasible.

A number of spectral lines have been identified whose spectral responses are algorithmic (mostly linear) over several orders of magnitude and with high sensitivities suitable for quantitative analysis particularly in the analytical range $0 \le 2000$ ppm (Table 6.4)

A casual survey of the lines revealed that the line to background ratios are commonly better than 5. This implies prospects for achieving good detection limits for each of the selected element lines, when typical sediment is analysed.

Most of the curves in Fig. 6.5 show good correlation between the analyte concentration and signal intensity, which is confirmed by the correlation coefficients of the regressions. The slope of the calibration curves varies from between 0.9909 to 0.9999 indicating a suitable analytically viable variation of the spectral signal versus species concentration in the matrix.

The respective spectral line preliminary estimates of the analytical figures of merit are [also] summarised in Table 6.4. The type of correlation, the [correlation] coefficient, and the approximate linearity range obtained from linear least squares regression fitting for the spectral lines are shown.

In the linear analytical range the analyte signal is normally assumed to exceed the nine-fold rms noise and the relative statistical error should be ≤ 5 %. However, non-linear calibration curves allow one to use the full analytical working range. Most of the nearly-linear lines that were not selected either showed spectral overlaps resulting from the other spiked species spiked simultaneously which had high blank values or they were not adequately sensitive; nonetheless such lines may be useful for analytical work in the absence of the interfering species lines, as for example in modified gas atmospheres, in analyses where the interfering elements are sure to be absent, or in the case of the utility of multivariate calibration with chemometrics in order to increase the reliability of quantitative evaluation.

The detection of arsenic, cadmium and mercury using sliding spark spectrometry are currently limited probably due to reduced excitation in an air plasma and to self-absorption or elemental fractionation during ablation. No suitable analyte line for the quantitative analysis of arsenic was found.

The prospective detection limits for these analytes may be much lower in pure nitrogen plasmas; the presence of even a small amount of oxygen in pulsed discharges degrades performance of detecting these elements by decreasing the excitation temperature – because they are volatile the excitation and spectral intensity acquisition parameters may not have enabled their optimum detection at this stage. In the case of arsenic, absorption of the short wavelength UV (200 - 400 nm) emission in which most of the intense lines of arsenic occur, by oxygen and related species, could be the main cause of lack of suitable quantitative spectral lines and the high detection limit shown for those lines identified and measured.

Element	Excitation	Pagragaion	Degregation	Approximate Apolytical Panga
Ling() (nm)	Excitation Energy (aV)	Eurotion	Coefficient	(ppm)
	5 20	Delemential		(ppiii)
Mn II 348.291	5.39	Polynomial	0.9980	2500
Mn II 344.198	5.37	Polynomial	0.9950	2500
Mn II 293.638	12.48	Polynomial	0.9943	2500
Mn II 260.569	4.75	Polynomial	0.9971	2500
Mn II 259.373	4.77	Polynomial	0.9901	1200
Mn II 257.610	4.81	Linear	0.9941	1200
Cu II 224.700	8.23	Polynomial	0.9928	>3500
Cu I 222.778	7.20	Linear	0.9951	3000
Cu II 221.810	8.41	Linear	0.9907	3000
Cu II 219.226	8.48	Polynomial	0.9936	>3500
V II 327.112	4.88	Polynomial	0.9985	2500
V II 313.333	4.29	Polynomial	0.9979	2500
V II 312.528	4.29	Polynomial	0.9992	2500
V II 311.838	4.31	Polynomial	0.9999	2500
V II 310.937	7.11	Polynomial	0.9989	1200
V II 297.226	6.54	Linear	0.9926	1200
Co I 350.228	3.97	Linear	0.9956	3000
Co I 345.351	4.02	Polynomial	0.9938	3000
Co I 252.897	5.48	Linear	0.9967	3000
Co II 237.862	5.62	Polynomial	0.9931	3000
Co II 236.379	5.74	Polynomial	0.9978	3000
Co II 230.786	5.87	Linear	0.9997	3000
Cr I 357.868	3.46	Polynomial	0.9994	2500
Cr II 336.804	6.16	Linear	0.9978	2500
Cr II 313.205	6.44	Linear	0.9946	2500
Cr I 284.602	7.80	Linear	0.9907	2500
Cr II 267.879	6.12	Linear	0.9969	1200
Ti I 498.173	3.33	Polynomial	0.9978	3000
Ti II 350.489	5.42	Linear	0.9978	1200
Ti II 338.783	3.68	Linear	0.9982	1200
Ti II 338.376	3.66	Polynomial	0.9958	1200
Ti II 334.188	4.28	Linear	0.9964	1200
Ti II 328.766	5.66	Linear	0.9996	2500
Ti II 323.452	3.88	Polynomial	0.9982	2500
Ni I 361.939	3.85	Linear	0.9982	2000
Ni I 352.454	3.54	Linear	0.9929	2000
Ni I 341.394	3.65	Linear	0.9992	>3500
Ni I 310.771	4.16	Linear	0.9923	2000
Al I 396.152	3.14	Linear	0.9915	>2500
Pb I 368.347	4.34	Linear	0.9977	>4000
Zn I 472.216	6.66	Linear	0.9959	>4000
Zn I 334.502	7.78	Linear	0.9979	>4000
Zn I 330.259	7.78	Linear	0.9960	>4000
Hg II 398.396	7.51	Polvnomial	0.9985	2000
Hg I 280.443	9.88	Linear	0.9981	>4000
Fe II 276.893	5.55	Polynomial	0.9928	3000
Fe I 274.111	7.74	Linear	0.9909	>3000
Cd I 228.802	5.41	Polynomial	0.9947	5000
Cd II 226.502	5.47	Polynomial	0.9919	1000
Cd II 214.441	5.78	Polynomial	0.9999	1000

 Table 6.4
 The spectral lines pre-selected for sliding spark quantitative analysis

F1	spectroscopy and th			
Elem.	Std. atomic lines/nm	Std. ionic lines	Lines detected	Lines selected
Mn	403.449 403.307 403.076	260.569	403.307	260.569
	280.108 279.827 279.482	259.373	260.569	259.373
		257.610	259.373	257.610
			257.610	
Cu	510.554	224.700	327.396 324.754 224.700	224.700
	327.396	219.226	327.396 219.226 213.598	219.226
	324.754	213.598		
V	440.851 439.000 438.472	312.528	312.528	312.528
	437.924 411.179 318.540	311.838	311.838	311.838
	318 398	310 230		
	510.570	309 311		
Co	<i>A</i> 12 132 <i>A</i> 11 877 300 531	251 082 238 802	352 981 350 228 346 580	352 981 350 228
0	352 081 350 228 346 580	237 862 236 370	345 351 341 234 340 512	345 351 237 862
	345 351 341 224 340 512	237.802 230.379	228 202 227 262 226 270	236 379 230 786
	545.551 541.254 540.512	230.760	230.092 237.802 230.379	230.377 230.760
C	520.842.520.602.520.451	228.010	250.780 228.010	220.010
Cr	520.842 520.602 520.451	286.092 285.567	360.532 359.348 357.868	300.532 250.249
	428.973 427.481 425.433	284.983 283.563	360.533 286.092 284.983	359.348
	360.532 359.348 357.868			357.868
То	500.721 499.951 499.107	338.376	499.107 498.173 399.864	499.107 338.376
	498.173 453.605 453.592	337.279	365.350 364.268 338.376	337.279 336.121
	453.558 453.478 453.324	336.121	337.279 336.121 334.903	334.903 323.452
	430.592 399.864 365.350	334.903	323.452	
	364.268 363.546	323.452		
Ni	361.939 352.454 351.505	228.708	361.939 352.454 351.505	361.939
	349.296 346.165 341.477	227.021	349.296 346.165 341.477	352.454
	305.082 300.249	226.446	226.446	341.477
		225.386		
Al	624.335 623.176 396.152	281.618	396.152	396.152
	394.401 309.284 308.215	266.917	394.401	
		263.155		
Pb	405.782 368.347 363.958	560.880	405.782	368.347
10	283 307 261 418 216 999	220 351	368 347	
	200.007 201.110 210.777	220.001	363 958	
Zn	636 235 481 053 472 216	255 796	472 216 468 014 334 502	472 216
2.11	468 014 334 502 330 259	250,200	330 259 328 233 255 796	334 502
	328 233 213 856	206 101	213 856	330 259
	528.255 215.850	200.191	215.650	550.257
Ug	546 072 425 822 404 656	202.331	366 333	
пg	340.073 433.833 404.030		265.015	
	500.525 505.484 505.015 252 652		303.013	
P.	233.032	275 574 274 022	274 500 274 556 272 490	
ге	440.475 438.355 432.576	2/5.5/4 2/4.932	3/4.590 3/4.556 3/3.489	
	430.790 427.176 406.360	259.940 241.331	3/1.994 358.119 2/4.932	
	404.582 379.851 374.590	241.052 240.488	259.940 239.562 238.207	
	3/4.556 3/3./13 3/3.489	239.562 238.207		
	3/1.994 358.119 302.064			
~ .	248.327			
Cd	643.847 479.991 361.051	274.858 257.293	361.051 346.620 340.365	228.802
	346.620 340.365 326.105	231.277 228.802	231.277 228.802 226.502	226.502
		226.502 214.441	214.441	214.441
As	289.871 286.044 278.022			
	245.653 237.077 236.967			
	234.984 228.812			

Table 6.5A comparison between the standard (sensitive) emission lines in atomicspectroscopy and the spectral lines detected and measured in the sliding spark

6.7 Discussion

The measurements presented in this chapter are an encouraging starting point to show how sliding spark spectrometry can be utilised for versatile quantitative trace element spectroscopy in non-conducting materials under modified matrix, and spark source discharge parameters.

By simultaneously inducing ablative atomic excitation that is spectroscopically measurable, the sliding spark technique allows the material's trace matrix components to be subjected to quantitative spectrometric investigations under simple external conditions.



Fig. 6.6 Preliminary sliding sparking tests on Rhine sediment bound in various matrix modifiers

The intensity-concentration correlation achieved, which is several orders of magnitude, is encouraging. A similar excitation efficiency in sediment samples may be assumed to be achievable. The validity of assuming halogenation in the sediments for the elements Mn, Fe, Co, which are contained in the sediment at trace concentrations, is demonstrated in Fig. 6.6.

Sliding spark spectrometry may thus be applied to the analysis of typical sediment samples. However, the use of the halogenation technique in enhancing the spectral excitation of the trace elements should be augmented by the careful optimisation of the atomisation and excitation processes based on the spark source opto-electronic parameters and spectral line-specific matrix modifier selection criteria. The following chapter is devoted to that task. This is because, unlike for the case of oxides spiked in a PVC polymer matrix, sediment is a complex matrix that is also highly refractory. Maximum accuracy and precision with minimum effort and cost are the major goals in the development of any analytical procedure.

7.0 Spark System and Analytical Method Optimisation

7.1 Rationale for Sliding Spark Optimisation

The potential for the sliding spark technique to perform trace element analysis is nonetheless still plagued by complex, mainly theoretically yet-to-be-understood analyte kinetics, which includes vaporization and atomisation effects in the difficult matrices. The matrix effects, like the spectral emission, are functions of sample chemistry and size of the ablated particles entering the discharge plasma. Thus they are matrix-dependent. For instance, sediment, like all siliceous materials, may undergo partial melting with the formation, during ablation, of glass [234]. This process results in variable vaporisation rates for the trace elements in the matrix. Simultaneous multi-elemental analysis under fixed spark source characteristics is therefore undermined by the wide variations expected in analyte atomisation due to non-uniform dissociation, particle-plasma interactions and other thermochemical processes. The spectral response functions so far measured utilizing trace elements embedded as oxides in the PVC may thus, depending on the analysed sample matrix, change significantly.

Assessment of the spectral data so far obtained and reported points to the need to better control the sliding spark excitation efficiency of the analysed matrix, and accuracy and precision in the trace element analysis in complex matrices. Representative atomic and ionic number densities in sliding spark discharge plasmas sustained by sediments differ significantly from those obtained in the PVC in each ablation.

Preliminary test spectra observed from simulated sediment bound in PVC indicated that the spectral line signal intensities suffer a reduction of several orders of magnitude as compared to spectra excited from the elements bound as oxides in the PVC under similar experimental conditions and equal analyte concentration. The factors that prevent spectral the responses of the analytes from being ideally algorithmic were discussed in Chapter VI.

As with all techniques, figures of analytical merit for the sliding spark are a function of numerous variables including instrumentation, operating conditions, sample, and elements being determined. The degree of analytical accuracy and precision depends upon the discharge current, inductance, initial rate of applied voltage, gas environment in which the spark is initiated, specific capacitance of matrix surface, and the mode of sample ablation.

This chapter aims to describe the procedures to minimise sliding spark source- and samplerelated matrix effects. Attention was shifted from the relatively simple case of the analysis of PVC embedding trace elements in their oxide form to the possibility for direct sediment analysis.

A detailed optimisation study using time-integrated, spatially resolved emission is presented. The influence of spark source opto-electric parameters, matrix modifiers, as well as ablation frequency on the sliding spark emission is investigated.

The objective was to improve the detection power of the sliding spark technique for direct quantitative determination of trace elements in palletised oxide-dominated solid dielectrics.

Capacitance	14 µF
Discharge condition:	'Hard'/ 'Soft'- variable depending on measurement
Scan time	600 ms unless must be varied for experimentation
Scans	11 (with 1 pre-spark for surface cleaning)
Electrode gap	4.5 mm
Intensity replicates	9
Spark shots per replicate	10-15
Intensity measurement	Counts accumulated during integration are automatically divided by the time of integration by the software

 Table 7.1
 General experimental conditions used in the optimisation measurements

7.2 The Optimisation Parameters

The peak and relative timings of the discharge current may be controlled in a variety of ways in order to study the manner in which these affect the analyte signals from a sample matrix having varying concentrations of specific elements under investigation. The measured (integrated) analyte emission properties simultaneously depend on spark source frequency, electrode geometry, and on both single-spot temporal and single-sample spatial distribution of the intensity signal.

Characterisation and monitoring of the spark source parameters with respect to the analytical signals can therefore reveal the causes of both sampling and spark-spark non-reproducibility. Previously unrecognised variables may also easily be noted and empirically controlled.

Spark source optimisation was undertaken with two aims. One, to find optimal compromise conditions for simultaneously exciting the heavy trace elements in typical non-conducting

samples. Two, to understand the various conditions for forming sliding spark discharges that result in intense, accurately measurable trace element spectral line signals.

For the sliding spark source electrical parameters the solution of two problems is important. The first is the maximisation of the pulsed deposition of the sliding spark energy into the plasma column. The second is the best method to modulate that energy deposition. The spark source electric parameters have been correlated with the spectral line intensities of trace elements spiked and bound as oxides in a PVC polymer powder (prepared in pellet form).

The study of the emission characteristics of the detected spectra was accomplished by the sequential optimisation of elements in groups of three, selected with respect to the following spark source parameters, which affect the analyte signal intensity emitted from the sample:

- The capacitance in the spark source, which influences the energy supplied to the plasma channel and to some extent, average amount of excitation and thus the emission intensity.
- The circuit inductance, which determines the power input into the plasma channel, and both the initial peak value and decay time for the individual discharge current.
- The source combination of capacitance, inductance, and resistance, which determines the spectrometer scan frequency and gives rise to specific ablation rates upon which the nature of the radiation and signal intensity strength from a given matrix is dependent.

The selection criteria used for the various groups of elements to be simultaneously analysed are best guided by similarities in ionisation potential, the vaporisation temperature of oxides, and the average excitation energy for the analytical lines (see e.g., Table 6.4).

7.21 Discharge Breakdown Voltage

When other factors such as the environment (temperature, humidity, gas) in which the sliding spark is initiated are kept constant, beyond the critical value 5 kV (for the \approx 4.5 mm interelectrode gap) the reproducibility of the spark emission (as reflected in the RSD values of measured intensity) only depends on the peak discharge voltage to a limited extent (Fig. 7.1).



Fig. 7.1 Dependence of measured line intensity on sliding spark source applied voltage for a 4.5 mm inter-electrode gap spark head

Although the discharge breakdown voltage in principle only depends on the dielectric strength of the underlying matrix and on its surface structure - both of which influence the electric field inhomogeneity especially at the cathode-sample interface - it can be observed from Fig. 7.1 (from the Mn II 259.373 and Ti II 338.376 lines) that changes in the spark source voltage can result in measured line intensities that may vary to as high as double in the short interval e.g. 5-7 kV, and 8-10 kV.

The relative signal intensity was computed by normalising to the highest value measured intensity for each line.

Element-dependent excitation in the plasma column core appears to be influenced by the degree of the initial (breakdown) electric field inhomogeneity at the cathode-sample contact.

Normally, in a free spark the breakdown voltage is $\approx 30 \text{ kVcm}^{-1}$ (in dry air), which means $\approx 15 \text{ kV cm}^{-1}$ for a 4.5 mm electrode gap. But due to the small cross section of the sliding spark, a high electric field potential drop is realised, which develops high power per unit volume concentrated in the narrow region along the surface of the analysed sample. For a given discharge annulus width Tawil [235] found that, the spark resistance decreases with increasing

capacitor voltage, until the current waveform is critically damped. The peak intensity for every spectral line, which depends on the elemental excitation efficiency, occurs at the critical damping voltage. This enables the discharge to proceed at a considerably lower static breakdown voltage, aided (and modulated) by field perturbations induced by the surface microstructure [22,35].

Because the streamer and spark stages have been observed to be absent in vacuum surface discharges, it may be postulated that breakdown in sliding sparks occurs as a result of cascade ionisation of the air layer adsorbed onto the surface of the analysed sample, close to the electrode.

In the voltage interval studied, the spread of measured intensities and the RSD values for the elements are minimum at 8–10 kV. It would be more instructive to perform quantitative monitoring of the voltage source drifts; this should provide better insight into sliding spark-applied voltage related effects, since the drifts are correlated to the chemistry of the discharge plasma, and their control can lead to increased intensity signal and precision, plasma channel stability, and other elemental and matrix-related properties.

7.22 Spark Source Capacitance

The capacitance in the spark source directly influences the power supplied to the spark gap, and to some extent the average amount of excitation obtained and thus the excited spectral line intensities. The energy stored by the capacitors, which is deposited in the sample surface layers during discharge, is equal to $0.5 \ CV^2$, where C is the total spark source capacitance and V_c is the breakdown voltage across the capacitors.

Energy dissipated in the plasma column across the sample surface can have direct analytical consequences. The correlation between the capacitance and spectral line intensity is shown in Fig. 7.2 a. The outliers in the figure are observed mostly at $6 \mu F - 8 \mu F$. This is because three capacitors ($2 \mu F$, $4 \mu F$, $8 \mu F$) are variously combined to obtain the different total capacitance: $2 \mu F$, $4 \mu F$, $8 \mu F$, $10 \mu F$, $12 \mu F$, $14 \mu F$ possible for the present spark source design.

The differences observed between Fig. 7.2a and Fig. 7.2b show however that the influence of capacitance on the energy deposited in the plasma channel is strongly moderated by the circuit inductance, which determines the strength of the discharge. Both inter-electrode (sample) gap impedance and energy dissipation, are a function of discharge current. It may be noted that for added-inductance ('soft') discharge (Fig. 7.2b) measured intensities are as low as 10 orders in magnitude as compared to non-inductive ('hard') discharges (Fig. 7.2a).



(a)



Fig. 7.2 Discharge strength-modulated dependence of sliding spark excitation emission spectral line intensity on the source capacitance

The results presented in Fig. 7.2 fit circuit theory, according to which the time at which the maximum discharge current observed increases with increasing capacitance (i.e., more energy is deposited in the plasma channel) but it decreases with decreasing inductance.

Clearly, adding inductance ion the circuit (chosen so the pulse impedance of the driver circuit and transmission conductors remain characteristically less than the load circuit elements and plasma column impedance) to the discharge has no effect on the discharge energy; but it does alter the temporal characteristics of the energy deposition in the discharge and therefore the measured spectral line intensities. Low inductance increases the peak current density and the rate the of energy deposition into the discharge plasma. It has been shown [115] that sample uptake is dependent and proportional to di/dt of the discharge current waveform, where *i* is the current induced in the matrix and *t* is the pulse duration, which is inductance-dependent.

7.23 Inter-Electrode Gap

In principle, for trace element analysis one must seek as high ablation mass as possible so as to result in high measured signal intensities suitable for quantitative analysis. (But high mass of ablated sample matrix is less appropriate for the determination of the minor and major elements). Trace element analysis by sliding spark spectrometry requires that a critical minimum mass of material be ablated to be able to achieve acceptable signal-to-noise ratios, and quantitative sensitivity. The emitted radiation can only be more intense because more material has been vaporised and consequently atomised, ionised and excited in the discharge.

Fig. 7.3 shows the effect of varying, while keeping the rest of the experimental conditions fixed (see Table 7.1), the electrode gap in relation to the detected emission intensities for selected spectral lines. The relative intensity was computed by normalising relative to the highest intensity measured for each line. The relationships are clearly, approximately similar; they may be described by an average polynomial function:

$$y = -0.0618x^2 + 0.5937x - 0.4761 \tag{7.1}$$

The wider the inter-electrode gap the more material is ablated and excited; but there is a critical limit to which the inter-electrode gap can be increased, at which the functions plateau out. For the spark head used in this work, this plateau occurs between 4–5 mm. This is because the extent to which the inter-electrode gap can be increased is limited by geometry: the solid angle of view for the radiation, subtended by the optical fibre utilised to collect and deliver the radiation emitted to the spectrometer optics, is optimally about 4.5 mm.



Fig. 7.3 Dependence of sliding spark emission intensity on spark source inter-electrode gap

7.24 Discharge Strength

As is noticeable from Fig. 7.2, there are significant differences in the strength of the intensity signals between 'soft' and 'hard' discharges at the different values of capacitance. These are due to the fact that adding inductance in the spark source affects the peak value of the discharge current, which determines the number of excited lines (and their intensities) that can appear in the spectrum (see Chapter VI). Studies performed on the imploding thin film plasma source (which is related to the sliding spark) have also shown that adding inductance to the discharge circuit produces a more homogenous plasma that is cooler and thus has different implosion mechanism than do low inductance discharges of the same energy [114,115].

But while added-inductance ('soft') discharges improve the emission characteristics, they are overshadowed by the poor atomisation properties of the plasma. Added-inductance ('soft') sparks are arc-like, that is, more material may be vaporised, but the average amount of excitation remains generally low. The emitted radiation can only be intense because more material has been vaporised, and additionally the discharge material has completely been atomised and efficiently excited.

As previously observed, sliding spark spectra from added-inductance ('soft') discharges show decreased background intensity and decreased spectral complexity. The emission lines in the added-inductance discharge spectra are also noticeably narrower.

Increasing the inductance increases the duration of individual discharges while at the same decreasing the initial peak value of the current. Normally, close to the time of peak discharge current the electron density reaches maximum. This maybe experimentally observed from time-resolved measured widths ($\Delta\lambda_{1/2}$) of the emission lines [1].

These characteristics are corroborated by the results in Fig. 7.4a & Fig. 7.4b, in which variable spark frequency (1–50 Hz) is introduced as a modulation parameter in the study of the dependence of spark source circuit capacitance on the measure spectral line intensities for both non-inductive ('hard') and added-inductance ('soft') discharges respectively. The dependence was examined for the elements Mn and Ti, for both neutral and ionic lines.

It was observed that for 'hard' discharges the most favourable conditions for efficient spectral line excitation are high (10–14 μ F) capacitance and low (0.5–10 Hz) frequency; the criteria being more applicable to the neutral than to the ionic lines.

It can also be observed that at high (35–50 Hz) spark frequency, high (10–14 μ F) values of capacitance are unfavourable for maximum energy deposition in the plasma column, since only low spectral emission line intensity signals are measured. For low (2–4 μ F) capacitance values, the intensity is independent of frequency.

For 'soft' discharges, the most favourable spark frequencies for efficient excitation are <2 Hz, and low ($<10\,\mu F)$ capacitance.

Thus, spark frequency may not be used to favourably (with respect to quantitative analysis) modulate the excited line intensities in added-inductance ('soft') discharges; the measured line intensities are still 4-5 orders of magnitude lower than those observed in the 'hard' discharges, independent of frequency. This effect is independent of the nature of the line considered: neutral or ionic.



Fig. 7.4a Scan frequency-modulated dependence of measured line intensity on sliding spark source capacitance for 'hard' discharges



Fig. 7.4b Scan frequency-modulated dependence of measured line intensity on sliding spark source capacitance for 'soft' discharges

7.25 Spark Scan Frequency

The principle correlations between the source capacitance, spark scan frequency, discharge strength and the emission signal intensity, which are shown in Fig. 7.4, may be summarised representatively using Ti in Fig. 7.5a,b and in Fig. 7.5c,d.

Fig. 7.5 shows, when all other conditions (see Table 7.1) are kept constant, signal intensity dependence on the spark scan frequency is independent of the spectral line considered.

The relationship between the source capacitance, spark scan frequency, discharge strength and emission signal intensity, however, is critically influenced by the source capacitance.

The apparent increase in the measured intensity is more pronounced at lower frequencies, gradually increasing with decreasing frequency for higher, than lower, values of capacitance.

This dependence is only applicable in the non-inductive ('hard') discharges. For addedinductance ('soft') discharges, the measured spectral line intensities are virtually independent of both the spark scan frequency and the source capacitance.

It can be observed from Fig. 7.5 (using Ti and Mn as examples), for instance, that the measured line intensities at 6 μ F and 14 μ F are almost the same for both 'hard' and 'soft' discharges, and are not affected by changes in the spark scan frequency.

In principle, for high sparking frequency (short spectrometer scan time) the next discharge is virtually superimposed on an already still slowly decaying discharge plasma. This has the effect to gradually increase the peak current value, which means the discharge strength would tend to be more "soft" (implying low intensity signal). It is noted that the degree of this induced 'softness' appears to particularly increase with increasing spark source capacitance.

Fundamentally, the character of the UV/VIS radiation emitted from the sliding spark should in principle depend upon the delay after spark ignition.

The observed results may be explained as follows:

The longer the scan time (low matrix ablation frequency), the greater is the interval up to the next sparking process (slower sparking sequence); therefore the longer the integration time there is for the spectrometer electronics to operate without memory effects.



Fig. 7.5a,b Inductance-modulated variation of ionic analyte signal intensity with source capacitance and scan frequency



Fig. 7.5c,d Inductance-modulated variation of atomic analyte signal intensity with source capacitance and scan frequency

This operation is necessary for reduced noise levels. Spark source memory effects derive largely from the current history just prior to the preceding discharge [129].

Essentially, the spark scan frequency determines the discharge burning duration.

Sliding spark sampling efficiency may in principle be increased by increasing the ablation repetition rate; but, besides memory effects consideration must also be given to the sample biases from pulse-to-pulse interactions, stemming from for example, spark-induced shock waves, or channel spreading.

7.3 Matrix Modifier Tests

It is well known that if volatilisation is to be used for the separation of the heavy 'impurities' from the light matrix with the aim of quantitative analysis, the 'impurities' should be either completely evaporated or a reproducible fraction should be evaporated [51].

The vaporisation of the heavy trace elements in sliding spark excitation has already been observed to be significantly increased in the presence of a halogen underlying matrix as compared to a non-halogen containing one, so favourable line detection in typical matrices is expected for samples bound in PVC or other halogen polymer matrix chemical modifiers.

The enhanced evaporation of trace elements observed for elements embedded in PVC in the oxide form is based on the potential of transforming the 'impurity' elements in the underlying base matrix into easily volatile halogen ides. A similar effect is observed for elements in oxide-type ceramics analysed using ETV [215] and DSI [219,236] techniques.

But so far, it is not clear as to whether the intensities for the heavy trace elements have spectral line-specific differences in the sensitivity of the signal enhancement in the different matrix modifiers. It is imperative to explore this possibility in the sliding spark. This may be done in two ways, both applicable to sliding spark spectrometry. One, examine the various sample binders (including non-halogen ones) for this analytical versatility. Two, explore, if any, spectral line-dependent matrix modifier characteristics (with view to optimising them).

Investigations were carried out to search for the most suitable matrix modifier for each element analysed and to infer how the different binder modifier matrices would influence the detected line intensities. The same experimental conditions summarised in Table 7.1 were used, except where the [respectively] investigated quantity is required to be varied. The results are shown in Fig. 7.6 (for elements spiked as oxides in the modifier matrices, at the concentrations indicated

in the respective graphs) and in Fig. 7.7 for the major elements in River Rhine sediment (bound in the various matrix modifiers in weight proportion of 1:1).

If sufficiently pure, the matrix modifier also acts as a diluent and sample binder.	
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Table 7.2	XRF-determined concentrations of the major elements in R. Rhine sediment					
Al	68.9	ppm				
Ti	3.94	ppm				
Mn	880	ppm				
Si	258	g/kg				
Fe	32.8	g/kg				





















Fig. 7.6b Further matrix-modifier spectral responses for trace elements spiked as oxides





Fig. 7.7a Influence of matrix modifier on the emission intensity signal detected from the major elements in a river sediment sample analysed using the sliding spark (I)



Fig. 7.7b Influence of matrix modifier on the emission intensity signal detected from the major elements in a river sediment sample analysed using the sliding spark (II)
The results reported in Fig. 7.6 and Fig. 7.7 show that teflon is a better matrix modifier for use in sliding spark spectrometry than PVC: Fluorination appears to be more thermodynamically favourable in enhancing the vaporisation of the heavy trace elements in pulsed discharge plasmas than chlorination, not withstanding the higher energy required to break teflon bonds in order to free the isolated fluorine atoms needed for the fluorination process. However, both are, for practical purposes, good matrix modifiers. The measured analyte signal intensities in teflon and PVC are high and differ significantly from those in borax and cellulose.

However for Al (Fig. 7.6a), Fe and Hg (Fig. 7.6b) no significant differences are noted in the measured spectral signal intensities between the matrix modifiers. Noteworthy is Hg in which the intensity of the most sensitive line detected in the sliding spark, Hg II 398.396, is measured in borax.

The results for Fe and Al are corroborated in Fig. 7.7a, where the spectral signal intensities from the major elements contained in River Rhine sediment were compared in PVC, teflon, borax, cellulose and quartz. The sediment was mixed in the matrices in weight proportions of 1:1. Because the major component of sediment matrix is quartz, the element concentrations in the resulting sediment-quartz mixture are in principle simply diluted to half of those measured in the pure sediment. For that reason the signal responses in quartz are not shown.

The spectral signal intensities for Al lines (Fig. 7.7a) are highest in teflon; no significant differences are noted for the signals in cellulose, borax and PVC. Fe shows a similar spectral response. A notable difference is observed in Ti: in the sediment–matrix modifier mixtures the highest spectral signal intensities are observed in teflon (for the other matrices the differences are insignificant). For the case of Ti spiked in the four matrices investigated the highest spectral signal intensities for the measured lines are observed instead in PVC, followed by teflon (the signals in borax and cellulose are insignificant in comparison). There are no significant differences between the spectral signal intensities observed for Si in PVC and teflon. These results seem to be in agreement with what was observed by Werner *et al.* [71]: Al and Si preferentially form fluorides as opposed to chlorides.

The above observation may not easily be attributed to possible spectral line saturation that is likely the case for the major elements measured in sliding spark spectrometry (for a more comprehensive discussion on this aspect see Chapter V). The phenomenon is noted for all the selected elements studied (summarised in Table 7.2) i.e., Zn, Co, Mn and V. It is therefore plausible to conclude that there is an apparent thermodynamic ease for fluorination for the sediment (as opposed to chlorination, which is the more energetically favourable halogenation process for the heavy elements embedded as oxides in the binding matrix). Noteworthy is the implicit possibility that not all the elements studied exist as oxides in the sediment.

It is not clear whether covolatization of matrix components during the evaporation of the relatively volatile elements like Cd, As, Pb and Hg, and the easy ones to vaporise such as Zn and Cu, is sufficiently attained. In Fig. 7.7b, it may be observed that the spectral signals intensities for the most sensitive line of Zn detected in sliding spark, Zn I 334.502, is not necessarily higher in teflon and PVC - in fact the strongest signal is observed in cellulose. This is probably because since 10 scans are integrated to obtain the intensity signals, cellulose presents a medium in which the signal does not deteriorate rapidly in the first few sparks scanned due to the relative volatility of the element (see section 7.4). ZnCl₂ and ZnF₂ may be so volatile that they evaporate from the matrix completely in the first few (including the cleanser) spark shots. A similar trend is observed for the highly volatile Si in the sediment (Fig. 7.7a), where the highest signal intensity is measured instead in borax. For some elements, the volatility may be lowered in the sediments owing to their chemical bond to different compounds; for example, As tends to be bound to iron [71]. In such case it is necessary to use a less-sensitive chemical modifier, which does not evaporate simultaneously with the elements to be determined, such as cellulose or borax, as observed.

It is noteworthy that these effects are directly observable in sediment owing to the low melting point of silicate matrices, and not the oxides (spiked) in the matrix modifiers studied.

It appears therefore that use of both PVC and teflon mixed in optimally-determined proportions as the matrix modifier is better suited for the efficient simultaneous excitation of the non-volatile heavy elements in sediments (in this way, simultaneous halogenation with chlorides and fluorides may sufficiently improve the evaporation of all the trace elements in the base matrix); while cellulose and borax suffice as matrix modifiers/binders for the volatile elements. The problem is that sample preparation with teflon is extremely laborious and delicate – the mixture of the sample and the teflon matrix has to be milled at liquid nitrogen temperature, and the rapid vapour that streams away upon evaporation is likely to drag some fine-sized sediment particles with it, leading to analyte loss.

7.4 Intensity Measurement by Single Spark Integration

It should be mentioned that it is not only high spectral line intensities (so as to ensure the registration of peaks of good counting statistics) with which to be concerned; the precision (measured in terms of the relative standard deviation (RSD) values of each intensity signal is of crucial interest). Single spark statistics is thus of greater importance in trace element analysis by sliding spark.

The spark emission is governed by the statistical fluctuation of the sparking process. This process can be represented by a Gaussian pulse height distribution where the excitation mechanism including the spatial fluctuations is the major contributor to the RSD. Essential deviations from the Gaussian distribution can normally be attributed to a non-homogeneous distribution of the respective elements in the sample [237].

In sliding spark spectrometry the phenomenon is much more complex. For each matrix analysed, one must strive to gain control of the elemental (as opposed to total matrix) efficiency in the sparking process in order to alleviate the problems associated with thermodynamics-related excitation statistics. For this reason spark source electronic control must be optimised to compromise between the number of sparks to be integrated (for the purpose of averaging out element-in-matrix inhomogeneity, including related analyte thermochemistry noise). Statistically noise $\propto N^{\frac{1}{2}}$, where *N* is the number of spark shots integrated. By modulating the scan time and number of spark shots (for each measured element line) to be integrated together into a single intensity measurement, one can minimise electronic noise while avoiding to spark the matrix to the extent of inducing carbonisation and sample ageing. Repeated sparking results in sample melting, reconstitution, condensation and differential partition of the matrix constituents between the melt, the solid and aerosol already dispersed in the discharge plasma. This, in simultaneous multi-element analysis using the sliding spark technique, complicates the intensity measurement statistics.

The relationship, at two scan frequencies 10 Hz and 5 Hz for both 'hard' and 'soft' discharges, between the sliding spark spectral line intensity and the number of single sparks integrated to obtain the analyte intensity is shown in Fig. 7.8 for Ti, V and Mn.

As can be observed, the relationship is independent of the nature of the spectral line, i.e., neutral or ionic, and only depends on the measured element involved (Fig. 7.8).

The intensity signal is more critically dependent on the number of sparks integrated, in the 'hard' than in the 'soft' discharge. It may be noted for instance for Ti that, the intensity signal obtained at 7 spark scans can be as high as twice that obtained at 2 spark scans. Beyond 10 spark scans, the measured intensity is independent of the number of sparks integrated. This phenomenon is, for 'hard' discharges, independent of the spark pulse frequency. For 'soft' discharge, although relatively low intensities (ten orders of magnitude less) are observed, the signals remain more or less independent of the number of spark scans integrated up to 10 spark scans; above this there is a sharp increase in the strength of the intensity signal measured. A similar pattern is observed for both V and Ti.

But for Mn, the intensity signal obtained at 7 spark scans for instance (Fig. 7.8) can be as low as half of that obtained at 2 spark scans. After 10 spark scans, for the 'hard' discharge, the signal stabilises, becoming independent of the spark pulse frequency. For the 'soft' discharge, although the signal is too low in comparison with that obtained in the 'hard' discharge, the dependence is similar to that observed in Ti and V.

These results depict the sliding spark ablation process and intensity measurement as very complex such that they require more comprehensive investigation.

An attempt has been made to study the evolution in time of the intensity signal for every element analysed. The results are reported in Fig. 7.9a and in Fig. 7.9b, according to which the time evolution of the signal has been confirmed to be element-specific. The results reported for Ti, Mn and V in Fig. 7.8 are corroborated by the spark-resolved, single-spot spectral measurements reported in Fig. 7.9a and in Fig. 7.9b. The analysed elements were spiked in groups of three at ≈ 500 ppm in the PVC, according to the conditions of Table 7.3.

	Spark source conditions
Source capacitance	14 µF
Discharge condition	'Hard'
Number of scans	30
Scan time	200 ms, 100 ms
Electrode gap	4.5 mm
	Element groups (spiked as oxides)
Group1	Al, Fe,
Group2	Mn, Ni, Ti
Group 3	Cr, Co, V
Group4	Zn, Pb, Cu
Group5	As, Cd, Hg

 Table 7.3
 Spiking scheme and analysis conditions for the spark-resolved measurements



Fig. 7.8 Dependence of sliding spark intensity signal on the number of spark scans integrated to obtain the measured intensity for selected elements and frequency

The time evolution of the sliding spark signals is caused by different physical and/or chemical states of the base matrix surface in relation to the more in-depth properties of the sample material which become continually exposed with every spark shot during sample ablation [238]. It is also caused by the preferential evaporation, because of the different and time-dependent saturation vapour pressures of the various elements embedded in the matrix.

Essentially, the sliding spark samples both by sputtering and bulk heating; once the sample material melts, the various elements, especially in a many–component refractory matrix, can be differentially dissolved and sampled at the liquid-solid interface. The molten material also resolidifies between the discharges so that there is an ageing effect when sparking continually to a single point on the matrix surface. This may cause carbonisation, which is matrix-dependent, being more severe in matrices with high carbon content. Many plastics and ceramics form carbonised conducting paths under the influence of surface discharges.

Carbonisation causes short-circuits in the plasma discharge column; the breakdown is no longer constrained and becomes explosive, and there is over-erosion of the ablated matrix surface, leading to unrepresentative sampling. The effect of carbonisation, which occurs at about the 24th spark, is observed in Ni, Fe and V as shown in Fig. 7.9a. The carbonisation process, as observed from these elements is preceded by a gradual decrease in the measured intensity signals. At the centre of the sparked area, the surface is re-melted; in this re-melted area, the sample surface is enriched in carbon and probably depleted of the other elements.

Time integration of sliding sparks normally means spatial integration over the sample, typically over a spot diameter 4-5 mm depending on the source opto-electric parameters. Each individual spark in actual fact forms a crater of approximately 10 to 30 μ m in diameter [238], so its emission represents only this small spot. By initially summing a certain number of single-spot sparks, the information on possible modulation by analyte volatility including inhomogenieties of the sample, is to a large extent lost, as can be observed from the intensity signal patterns for most elements reported in Fig. 7.9a and in Fig. 7.9b. For the volatile elements (in their chloride and fluoride form) in the analysed matrix, the first emission pulse is the most intense; the intensity signal of the successive pulses decreases more rapidly than it happens in the case of the non-volatile heavy elements in the same chemical form.



Fig. 7.9a Spark–resolved single-spot spectroscopy: evolution of 'hard' intensity signal with spark sequence scan number at 5 Hz, with spectrometer delay time (I)



Fig. 7.9b Spark–resolved single-spot spectroscopy: evolution of 'hard' intensity signal with spark sequence scan number at 5 Hz, with spectrometer delay time (II)

However, the signal evolution appears to be a more thermally complex process. For instance, for elements like Fe and Ni, the intensity signal is statistically constant in the first 10 sparks. V lines show a gradual increase before stabilizing at about the 8th spark, while for the rest, there is a variation in the degree of the gradual decrease in the measured intensity signal; for some elements like Ti, Mn, Co, Zn, Cu and Pb, the intensity signal decreases to half of that initially observed within the first few (about 8 on average) sparks, before stabilizing.

The effect is independent thus of the volatility of the element as known in the free atom state. This appears to show that, if one were to attribute to sample inhomogeneity only, the statistical fluctuation in the measured intensity signal and RSD values, it would imply the analysed element is more homogeneously distributed in the underlying surface layers than on the sample surface. Since this is untrue, element-specific thermochemical properties, which are matrix-dependent, play a role; in the meantime it would be sound analytical practice to optimise in terms of spark number the intensity signals that should be integrated for each element in order to obtain the highest signal-to-noise, and signal-to-background, ratios. In that case, measuring the intensity signal when it has temporal stability may be less preferable to integrating only two or three sparks per spot, then summing it instead over the sample surface.

7.5 Particle Size Effects

If it can be assumed that the limiting noise in sliding spark spectrometry is in principle the stray plasma light scattered within the discharge plasma plume by the ablated sample particles, particle size becomes important because the interaction of the ablated particles with the discharge plasma depends on both the size and composition of the major components of the matrix. Particle size is also related to the sample heterogeneity, which affects the emission signals due to the fact that relatively small particle size is required for efficient atomisation.

The test elements were spiked in simulated sediment prepared according to the scheme shown in Chapter VIII (see Table 8.3) as oxides so as to result in element concentrations of \approx 750 ppm. The simulated sediment, embedding the analyte, was then mixed with PVC powder in weight ratio of 3:1 (simulated sediment: PVC). The mixture was machine-ground as described earlier (see section 5.7) for three hours. Before pressing into pellets the powders were sieved into 6 different particle sizes as indicated in Fig. 7.10 and then analysed according to the experimental conditions summarised in Table 7.1.

From Fig. 7.10 it is clear that both the atomisation efficiency of the analysed elements in the sample and in the discharge plasma are affected by the particle size of the constituent minerals and the dimensions of the ablated particles and aggregates in the simulated sediment.

No significant enhancements of the intensity signals are noted, as expected, for the fine-grained particle-sized samples. It would appear the elemental spectral line signal intensities are less responsive to decreases in particle size, because the signal intensity is enhanced with increasing particle size up to 90 - 125 μ m diameter. For volatile elements such as Cd, this dependence is less pronounced. Noteworthy is the correlated extent of the intensity increase with decrease in RSD as the particle size increases.

This increase in intensity may be related to the binding properties of PVC matrix modifier. During sample preparation it was noted that the finest ground sample powder (< 20μ m) could not bind well, which indicates that less of the binder (PVC) matrix exists at this particular particle size. This is confirmed by the high (> 15 %) values of RSD measured at that particle size in the sample. Nonetheless for the rest of the particle sizes the RSD is well below 15 %, averaging about 10 % and lower (which is acceptable for good precision measurements).

This is confirmed by observing both the intensity and RSD values for Cl. A similar pattern is noted for the RSD, which confirms that the distribution of PVC particles in the fine-grained sample is not only limited but also inhomogeneous (as a result). This, entirely uniform correlation between sample particle size and both the intensity signal and the RSD of its measurement are noted for the other elements analysed viz., Cu, Si, and Cd (Fig. 7.10). The RSD values seem to be more dependent on the binding capacity of the PVC than on the particle size for all the particle sizes examined. Except for < 20 μ m particle size, the RSD remains ≤ 10 % for all the particle sizes 20–125 μ m.

No significant differences are observed in this relation between volatile elements (e.g. Cd and Si) and non-volatile elements (e.g., Cu and Ti). Normally, the intensities of refractory elements are expected to be more sensitive to particle size than the volatile elements. The intensities of the former should in principle sharply increase with decreasing particle size and their atomisation efficiency (and possibly ablation rate) in fine-grained samples, and is higher in the more amorphous than in crystalline silicates.



Fig. 7.10 Dependence of elemental spectral intensity signal strength and precision of its measurement on the particle size of the sample matrix for selected elements

However the behaviour of solid particles is not as easily understood as that of aqueous aerosols. A more comprehensive approach to predicting particle size effects in sliding sparks is required. The above observation is not in accordance with the interpretation of the intensity enhancements due to higher atomisation efficiencies expected for fine-grained particles. At present, there is no adequate experimental data to explain the behaviour. In the meantime, it may be postulated that a sample made up of fine-grained particles bound in PVC has higher sputtering /and ablation rate than coarser grade sample. Nonetheless, the observed particle size effects may easily be compensated for in the calibration by use of internal standards.

7.6 Ablation Characteristics

Although the thermal interaction of the sliding spark discharge plasma with the sample may be reduced with a state-of-the-art new excitation source, there is the possibility to tailor spark discharges that would reduce further the extent of melting and enhance representative physical ablation process, by studying the channel sampling and channel development as a function of the spark source parameters. The results are summarised in Fig. 7.11.

It may be desirable to find some responsive means to adjust the energy to allow 'controlled' ablation in various materials; that is, to form reproducible ablation pits.

However, contrary to metallurgical samples where homogenous ablated particles are formed, in the case of non-conducting materials, ablation processes differ from matrix to matrix. This is due to the more uniform and preferential ablation of the conducting material in contrast to that of the non-conducting refractory materials. Powders also contain abundant surface adsorbed species (primarily H₂O, CO₂, and hydrocarbons) and occluded atmospheric gases in the pore spaces; these in sliding sparks may contribute significantly to the spectral interference and to the background spectrum.

At the outer part of the sparked area, there are small localised spots hit by the discharge. It is generally accepted that the discharge preferentially hits edges of inclusions with a smaller electron work function in the matrix [239].

It has on the other hand long been recognised that not all elements exhibit the same emission characteristics during ablative sampling, since significant fractionation of elements may occur [79]. Fractionation is a dynamic process; in sliding sparks the degree to which it occurs during ablation is dependent on a number of factors: energy deposited in the discharge plasma channel, ablation frequency, and pulse width of the breakdown discharge current. Fractionation is normally more severe in low energy, high frequency sampling discharges.

Deterioration of the sample surface results from ionic bombardment, chemical attachment from the activated ambient gas or the plasma reaction products, and vaporisation due to radiative heating. The different intensity patterns previously observed, derive from point-to-point variations in the ablated particles entering the discharge plasma. There is a likely re-distribution of elements in the surface layers caused by the spark discharge. Large interference, including from matrix and air molecular band lines, complicate the pattern so that the background also shifts as the major constituents change. This means the formation of a discharge on the surface of the sample depends on matrix chemistry and properties, e.g. dielectric strength, conductivity, chemical composition (changes in the surface composition alter sample electrical behaviour).



(a)



(b)

Fig. 7.11 Sliding spark ablation characteristics and channel spreading as a function of spark scan frequency, capacitance, and discharge strength

The sampling efficiency is defined as the amount of atomised material introduced into the plasma per unit time. If the sampling efficiency changes, corresponding changes in emission intensity in the plasma column will result, since different amounts of material are introduced into the discharge. For solid and powder samples, the amount of sample erosion increases with the amount of charge delivered into the surface for given period of time (Coulombic integral) and it also depends on the physical and chemical nature of the sample matrix. The relationship between sample ablation and Coulombic integral was investigated by Mohamed *et al.* [240].

Samples labelled 1	4 (Fig. 7.11a)
<u>Fracuency</u>	5 Hz
Scone	10
Discharge	Hord
Conscitance	$2 \dots E(\# 1) \in (\# 2) = 10 \dots E(\# 2) \text{ and } 14 \dots E(\# 4)$
Capacitance	$2 \mu F (\# 1), 0 \mu F (\# 2), 10 \mu F (\# 3) and 14 \mu F (\# 4)$
Samples labelled 5 –	<u>8 (Fig. 7.11a)</u>
Frequency	5 Hz
Scans	10
Discharge	Soft
Capacitance	2 μF (# 5), 6 μF (# 6), 10 μF (# 7) and 14 μF (# 8)
Samples labelled 10,	11, 14, 15 (Fig. 7.11b)
Frequency	40 Hz
Scans	15
Discharge	Hard (# 10, 11)
Discharge	Soft (# 14, 15)
Capacitance	6 μF (# 10), 6 μF (# 14), 10 μF (# 11), 10 μF (# 15)
Samples labelled 9, 1	2, 13, 16 (Fig. 7.11b)
Frequency	2 Hz
Scans	15
Discharge	Hard (# 9, 12)
Discharge	Soft (#13, 16)
Capacitance:	2 μ F (# 9), 2 μ F (# 13), 14 μ F (# 16), 14 μ F (# 12)

Table 7.4	The experimental	conditions for	generating	spark channe	el spreading images
			~ ~ ~		

From the pictures it may be noted in both Fig. 7.11a and in Fig. 7.11b that the degree of sample ablation, which may be assumed to be related to channel spreading is higher for 'soft' than 'hard' discharges. It increases with increasing capacitance, and it is more pronounced at higher source capacitance. For instance, in Fig. 7.11a, it is only possible to spark, without spark overlap, 4 spots on sample # 8 (14 μ F, 'soft'), while on the same surface area on sample number 5 (2 μ F, 'soft') it is possible to shoot 7 (and possibly more) sparks without overlap.

The corresponding case for the 'hard' discharge (sample # 4 and 1 respectively) have comparatively a lesser degree of channel spreading as compared to the 'soft' discharges under the same conditions of frequency and source capacitance. The number of spark scans used has some influence on the sample ablation and spreading (except when carbonisation occurs).

In Fig 7.11b, for instance only 3 sparks, with severe 'burning' are scanned for samples 15 and 16, both of which were made under 'soft' discharge and 14 μ F but at 40 Hz and 2 Hz respectively. This shows that the 'burning' depends more on the discharge strength and the number of spark scans than on the spark scan frequency employed.

In both Fig. 7.11a and in Fig. 7.11b, for instance, it is clear that sparks made under 'soft' discharge are much more darker (more sample burning and channel spreading) than those made under 'hard' discharge. The channel spreading (departure from cylindrical column symmetry) is more clearly demonstrated in the 'soft' discharge, than in the 'hard' discharge; and for both discharge conditions it has a frequency dependence.

Theoretically, the maximum size of the channel is reached at the same time as the maximum value of the current. Radiation from the highly ionised high-temperature cylindrical plasma column in the sliding spark, unlike in the free spark, is intercepted by the sample surface.

Because of surface vaporisation, the conductivity of the plasma channel becomes largest near the surface, and the channel quickly becomes asymmetric with higher expansion velocities parallel to the surface than perpendicular. The plasma can thus be described as ribbon-like rather than cylindrical [23].

7.7 Discussion

Sliding spark emission is thus a very complex process to modulate; it consists of spark formation (ignition) followed by the discharge current as a time function, sample ablation, excitation and ionisation of the sampled vapour, and finally the transmission of the emission into the

spectrometer. Spark-to-spark emission trajectories have been observed [35], but the investigation of the role of plasma in the spark-to-spark patterns has not been well-researched.

The understanding of the mechanisms governing the fluctuation of the single spark may help to decrease the RSD of the analytical measurement. If the fluctuation of the intensity follows a Gaussian distribution, the RSD of N integrated single sparks may be written thus [240]:

$$S_{i} = S_{SSE} / N^{\frac{1}{2}}$$
(7.2)

where S_{sse} is the RSD of the single spark intensity. The function describing only a single spark emission intensity from spot to spot is already a complex expression, represented as [51]:

$$\Delta l_{ej}(t) = k_{ej}(t) \Delta m_j(t) c_e(r v_j) \Delta t$$
(7.3)

The complexity is shown in Fig. 7.12. It may be noted that the excited tungsten electrode W I 345.075 and W II 343.722 emission lines have a better spark-spark reproducibility than those measured from the elements, which are spiked in the sample matrix. This means the sample inhomogeneity is a greater cause of signal irreproducibility in the sliding spark than is spark-plasma fluctuation. Signal variations could also result from sample depth-dependent ablations.

This underscores the method used to measure the analyte intensities. Spectral intensities from the average of 9 replicates were measured over fixed steady-state periods. Each intensity measurement is thus the result of integrating the radiation emitted from the discharge plasma over 90 (i.e., 10 single-spot x 9 replicate) shots. The intensity counts accumulated during integration are automatically divided by the time of integration by the application software.



Fig. 7.12 Single-shot spark-resolved (5 Hz – with spectrometer delay time) spectra showing random ablation-dependent spark evolution of sliding spark emission

Each single intensity signal process is dependent on the individual spark *j*. Δt is the time interval around *t*. The excitation function $k_{ej}(t)$, is a lumped factor containing the influences of the analyte density in the plasma, of the population density of the excited level, its transition probability, and the detection efficiency of the spectrometer. k_{ej} and the sample matrix ablation rate Δ_{mj} are dependent on the time *t*, where as the concentration in the sample $c_e(rv_j)$ connected with the line *e*, depends on the location vector rv_j .

Each spark *j* ablates a certain sample mass m_j stemming from the location rv_j on the sample surface. There, there exists a local concentration of the element, represented by *e*, which experiences the (averaged) excitation function k_{ej} . If the emission $\Delta l_{ej}(t)$, which is time-dependent, is integrated over the duration of a single emission, one obtains:

$$l_{ej} = k_{ej}m_jc_e(r\nu_j) \tag{7.4}$$

Eqn. 7.3 and Eqn. 7.4 imply that the factors k, m, and c if fluctuating, are independent of each other, which is not exactly true. In fact the ablated mass and actual concentrations in the sample do influence the plasma conditions and, consequently, the excitation function.

The sliding spark technique uses the integration mode for evaluation of the emission line intensity, averaging the accumulation of a larger number of spark events to form the intensity value representing the concentration of a given element in the sample.

Such an intensity consists of the sum of the emission pulses of numerous spark discharges. Therefore these intensities are already averaging the individual spark events, which are distributed over a certain diameter on the sample surface. The reproducibility of the integrated intensity which one experimentally observes is the result of both the fluctuation of the emission of the spark plasma and of the inhomogeneity of the elemental concentration in the sample (see Fig. 7.12).

Table 7.5	Summary of the	optimizable q	uantities in sl	iding spark	spectroscopy
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Ablation volume and mass of sample	
Analysis scan time (sample ablation frequency)	
Number and choice of elements to be detected simultaneously	
Elemental sensitivity in the matrix modifier	
Elemental background in the matrix modifier	
Elemental excitation efficiency	
Number of intensity scans to be integrated	

7.7 Conclusions

The results presented in this chapter demonstrate that in the UV-VIS spectral range a simple set of analytical conditions and spark source parameters exist, for the optimum attainment of spectral emission line intensities and signal-to-background ratios in sliding spark-produced plasmas. These conditions, if utilised, can lead to greatly improved detection power of the heavy elements in typical non-conductor powder matrices prepared as pallet samples.

The present study can however only be taken as an attempt at optimisation. From the results obtained, it is evident that in the sliding spark spectrometric analysis of non-conducting powdered solids there are dramatic structure-related matrix effects, but which are also element-dependent, which may render the analysis of pelletised samples extremely complex.

Although the sliding spark spectrometer in its present design has shown potential for trace element analysis of non-conducting materials, time and spatial discrimination techniques are still necessary in order to control and modulate the measurement parameters.

It is difficult to describe in detail, mechanisms of the observed sliding spark patterns including the matrix effects, without a more comprehensive optimisation study, preferably based on gated, fast time-resolved measurements combined with SEM imaging, and variable inductance modulation, including detailed statistical analyses of single spark emissions.

To understand the ablation effects demands to build a simple mathematical model of the atomisation process. The model may be based, for instance, on the assumption that the ablation rate at each point of the erosion crater is determined by the local phase composition.

If well empirically understood, an accurate knowledge of the various parameters of the spark source charging and sparking circuits, could then be described by models whose influence on the analyte signals can give insight concerning better-tailored excitation waveforms.

By assuming that the spark discharge is cylindrically symmetric, spectrally-resolved radial emission profiles could be calculated by Abel transforming the lateral emission profiles.

Nonetheless even with the modest experimental results obtained in this chapter, it can be concluded that discharge parameters, for instance peak current, current pulse duration, energy released into the gap, exert a strong effect upon the excitation conditions and processes of material entry into the discharge circuit, so it is desirable to have empirical control upon them.

If conditions for uniform and stable ablation rates are obtained, it means ablation can be performed either at a fixed spot or during sample displacement (translation, rotation) – this should increase the robustness and potential for sliding spark spectrometry in applied analysis.

Sampling statistics are an important aspect in sliding spark spectrometry especially when samples of heterogeneous materials such as rocks need to be analysed. Large variances can easily result when determining elements which are highly concentrated in a given mineral; for instance some elements, rather than being homogeneously distributed in the sample, are usually present in randomly disseminated nuggets of the highly concentrated elemental form.

Meanwhile a set of optimisation parameters has been identified for the optimal excitation of the analyte spectral lines in the simultaneous multi-elemental analysis using the sliding spark (Table 7.6). The optimal conditions are defined as those which produce a maximum intensity signal for a given analyte with correspondingly minimum precision RSD while other parameters are held constant. A sliding spark source that is optimised with respect to a specific group of spectral lines of elements of analytical interest realises the full utility of the analytical technique.

Scan time	100 - 200 ms (i.e., scan frequency $5 - 10 Hz$)
Source capacitance	$10-14 \ \mu F$
Number of scans	Element-dependent
Discharge condition	'Hard'
Electrode gap	4 – 5 mm
Number of pre-sparks	0 (i.e., not recommended)
Matrix modifier	PVC (for refractory, oxide dominated materials)
	Teflon for siliceous materials (sample homogenisation at liquid
	nitrogen temperature)
	Cellulose/borax for volatile elements in siliceous materials
Nature of analysis	Simultaneous, separate excitation for select groups of elements,
	depending on the analysed matrix

Table 7.6Optimisation conditions and parameters for efficient simultaneous excitation of
trace elements in sliding spark spectroscopy

VIII

8.0 Calibration Strategy and Quantitative Analysis

8.1 Overview

The primary characteristic for the successful application of sliding spark spectrometry in quantitative analytical work is the degree to which the measured spectral line intensity of the neutral or ionised species detected via their emission spectra scale up with the concentration of the parent atoms in the analysed dielectric base matrix.

While it is theoretically possible to calculate an analytical model for quantitative sliding spark spectroscopy from first principles, in practice there are several constraints, including the optical spectral collection efficiency, which are not explicitly known.

In spark-generated plasmas the measured intensities of spectral lines emitted by the constituent elements of a multi-element matrix are not, in general, proportional to the relative concentrations of the elements. The non-proportionality arises from complex interactions within the discharge plasma among which the presence of any one element can affect, owing to collisions, transition rates between states in other constituents. Consequently calibration is required if the emission spectra are to be used for accurate quantitative analysis.

At low analyte concentrations in the base matrix however, it has already been shown how the relationship between intensity and composition for the 14 elements analysed, excited in PVC, can be described by a simple power law over the trace concentration range. LTE, therefore, holds in the sliding spark plasma and self-absorption is negligible (i.e., the plasma is optically thin). For LTE to occur, collisions in the sliding spark discharge plasma must dominate the other energy transfer processes (viz., radiative decay and recombination), establishing a Boltzmann distribution among the bound energy levels, since the radiative lifetimes of these levels tend to be short and their collisional cross-sections are small [241]. It is justifiable therefore, to express, the spectral integrated line intensity I_q corresponding to the transition between energy levels E_i and E_i of the generic atomic species q with a concentration C_q , as:

$$I_q = FC_q \frac{g_i A_{ij} e^{-E_i/\kappa T}}{\mu_q(T)}$$
(8.1)

where T is the plasma temperature, $\mu_q(T)$ is the partition function, κ is the Boltzmann constant, g_i is the statistical weight of the *i*th state degenerate levels, A_{ij} is the Einstein spontaneous

emission transition probability into level j, and F is a constant depending on experimental and spark source conditions (see section 4.32).

A first order approximation of the concentration can be obtained by comparing the intensity of a given line from an unknown sample to that from a certified sample. Upon the hypothesis of small variation in the plasma temperature and concentration, all factors in Eqn. 8.1 are common except for concentration and line intensity for each analyte. This allows a simple linear relationship to be established between the specific line intensity and the relevant analyte concentration. Eqn. 8.1 thus allows to develop calibration strategies for quantitative analysis.

8.2 Practical Approaches to Quantitative Analysis

Generally, the detection of analyte species in sliding spark spectrometry leads only to 'relative' emission intensities; absolute values can be obtained only through knowledge of the spectral beam characteristics, of the spectroscopic constants involved in the process, and the careful calibration of the detection system.

It may be observed from Eqn. 8.1 that the integrated line intensity depends linearly, through the constant F, on the plasma density; so, an increase of the accuracy in the estimated element concentration based on a specific calibration model may only be achieved by using a reference sample with thermal properties as close as possible to those of the unknown sample in which one wishes to determine the analyte and its concentration.

Including the plasma temperature in the quantitative analysis allows to improve the overall accuracy of the quantitative prediction. By expressing the line intensities originating from the sample and a selected reference material (with known elemental concentration), at temperatures T_q and T_p , respectively, as a ratio, one obtains (from Eqn. 8.1):

$$\frac{I_q(T_q)}{I_p(T_p)} = \frac{C_q e^{-E_i/\kappa(1/T_q - 1/T_p)}}{C_p \mu_q(T_q)/\mu_p(T_p)}$$
(8.2)

Eqn. 8.2 allows to evaluate C_q from measured line intensity, while the other parameters may be derived from the literature of atomic data at known plasma temperatures. In order to estimate the plasma temperature one uses the relation

$$\ln \frac{I_q}{g_i A_{ij}} = -\frac{E_i}{\kappa T} + \ln \left[\frac{C_q F}{\mu_q(T_q)}\right]$$
(8.3)

which can be obtained by taking the natural logarithm of Eqn. 8.1 (see also section 4.4).



Fig. 8.1 Conceptual flow-chart for the semi-quantitative computation of the concentration of elements detected by the sliding spark technique based on measured relative intensities

In the two-dimensional (Boltzmann) plane identified by the LHS term of Eqn. 8.3, and by E_i , different emission line intensities belonging to the same element in the same spectrum lie along a straight line with a slope of $1/\kappa T$ (see Fig. 4.8).

If experimental and theoretical data are available for each element in the sample, the combined use of Eqn. 8.2 and Eqn. 8.3 makes it possible to evaluate element concentrations.

A conceptual scheme that is possible to implement based on semi-empirical computational techniques is shown in Fig. 8.1.

Alternatively, analytical models may be generated, based on two approaches: direct measurement of the spectral line intensities, and the internal standardisation procedure.

The goal of calibration for quantitative spectrochemical analysis is to find a mathematical relationship between the response metric extracted from the detected spectrum, and the desired property; i.e., between the analyte signal intensity and its concentration in the real samples. The main challenge is to structure the calibration in a form that can be expressed as a mathematical problem. The mathematical relationship is called an analytical model.

8.3 Calibration Strategy

8.31 Theory

Most analytical procedures involve linear regression either of the two calibration modes: *standard addition method*, or the *calibration curve* mode. Classical, i.e., non-weighted, linear regression is by far the most widely used regression method in either mode.

8.311 Classical Linear Regression

In conventional analysis, the *dependent* concentration variable, *x*, is correlated to the *independent* response variable, *y*, according to:

$$y = bx + a \tag{8.4}$$

For non-weighted regression, the slope, b, and intercept, a, of the regression line are given by

$$b = \frac{\sum_{i} x_{i} y_{i} - n \overline{x} \overline{y}}{\sum_{i} x_{i}^{2} - n \overline{x}^{2}}$$
(8.5)

and

$$a = \overline{y} - b\overline{x} \tag{8.6}$$

respectively where *n* observations (x_i, y_i) have been made, and where $(\overline{x}, \overline{y})$ is the centroid (mean) of the data defined by

$$\overline{x} = \frac{1}{n} \sum_{i} x_i$$
 and $\overline{y} = \frac{1}{n} \sum_{i} y_i$ (8.7)

respectively. For *standard addition* evaluations, the sample concentration, x_s , is predicted from the relation:

$$x_s = -\frac{a}{b} \tag{8.8}$$

and for *calibration curve* evaluations by:

$$x_s = \frac{y_s - a}{b} \tag{8.9}$$

where y_s is the observed response for the sample, and like was done in the work reported in this dissertation, where multiple measurements have been performed on the sample, the mean of the response values.

8.312 Weighted Linear Regression

Linearization of variables before calibration may be used to make the calibration model less complicated. For weighted linear regression based on the variance, s_i^2 , for the independent variable, the weight, W_i , for each point is given by [242]:

$$W_{i} = \frac{1/s_{i}^{2}}{\frac{1}{n}\sum_{i}\frac{1}{s_{i}^{2}}}$$
(8.10)

and slope and intercept respectively by

$$b = \frac{\sum_{i}^{i} W_{i} x_{i} y_{i} - n \overline{x}_{w} \overline{y}_{w}}{\sum_{i}^{i} W_{i} x_{i}^{2} - n \overline{x}_{w}^{2}}$$
(8.11)

and

$$a = \overline{y}_{W} - b\overline{x}_{W}$$
(8.12)

where the point (x_w, y_w) is the weighted centroid (mean) defined by

$$\bar{x}_{w} = \frac{1}{n} \sum_{i} W_{i} x_{i} \text{ and } \bar{y}_{w} = \frac{1}{n} \sum_{i} W_{i} y_{i}$$
(8.13)

Weighted linear regression analysis can also be based on the square of the independent variables y_i^2 . From the practical point of view the two approaches yield the same result if the relative standard deviation is constant, as this results in s_i being proportional to y_i .

Non-linear calibration models may also be used, but they require more complicated mathematical formulae.

8.313 Standard Addition and Set of Standards Calibration Methods

The standard addition method (SAM) is an often used, and well-known approach in instrumental analysis. SAM seeks to express the measured dependent variable as a linear function of the independent variables. The method is especially useful when the matrix effects occurring in the analytical system are unknown or relatively complex, hence causing difficulties in matching the matrix components in standards in the attempt to eliminate them. The calibration procedure consists of the addition of known amounts of analyte into a constant amount of sample, and measurement of the analytical signal for total analyte in each portion [243]. By doing so, the matrix components usually affect the signal proportionally to the analyte concentration, and the matrix effect is able to be compensated.

A weighted least squares fit of the function is carried out in successive approximation to determine the best values of the sensitivity and blank response; the calibration line extrapolated to zero signal is able to provide more accurate analytical results than those obtained from the interpolative calibration approach, although this method has important advantages like less random errors. (From the point of view of flexibility, sample preparation and analysis, sets-of-standards calibration method is however superior to SAM).

If the spectral signal versus the analyte concentration response is non-linear, SAM worsens in terms of precision. The non-linearity in the plot results from optical thickness of the discharge plasma, which leads to self-absorption and line reversal, and to the alteration of the scattering cross sections of the analyte atoms. Further, if the error in the spiked analyte concentration is not negligible, linear-least-squares and uncertainty estimates become very complex to fit.

There are other sources of error, mostly systematic, in sliding spark spectroscopy [244]. These include biased blanks, contaminated standards, wrong assumption of a given functional relationship, deficient data treatment, different analytical response towards different species of a given analyte (for instance, metallic ions in the free state or complexed with matrix), etc. Use of several element additions does to improve the accuracy of the analytical model [242].

8.4 Analytical Model Inter-Element Correction Factor

Where there is slight, known spectral interference, inter-element correction (IEC) may be performed manually or by the instrument software. For instance, to compute the interference correction for the Ti II 350.489 line from V II 350.443, a set of calibration standards may be prepared as shown in Table 8.1 and used to determine Ti from the resulting working curve. An interference-free Ti line is then used to also determine Ti. By comparing this interference-free concentration, with that obtained from the interference line, an IEC factor is computed.

	Concentration (ppm)							
	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7	Std 8
Ti II 350.489	0	10	40	200	2000	50	2500	2000
V II 350.443	0	10	40	200	50	100	20	10

 Table 8.1
 Example of calibration standards for analysis with interference correction

IEC is critical for trace element analysis where analytically useful lines are scarce. A number of the analytically useful lines (typed in bold) selected using PVC binder were found to have interference, which can affect the accuracy of the results during simultaneous analysis. The lines are shown in Table 8.2. The lines underlined are in principle possible to resolve with the present spectrometer, but electronic drift, and uncertainty in the peak identification (for small peaks) by the software can easily lead to unexpected spectral interference.

The sensitive lines of the common elements in sediment are included in Table 8.2. However, the list of interference lines from sediment is not exhaustive; sliding spark spectra are matrix-

specific and line-rich, and as was observed for the elements spiked in PVC, besides the most sensitive spectral lines many more lines are detected. Only empirical verification of every element in sediment can provide adequate evaluation of likely interference.

Analytical line/nm	Interference line
V II 312.528	Cr II 312.502
Co II 345.351	<u>Ti II 345.247</u>
V II 310.937	<u>Ni I 310.771</u>
Ti II 350.489	V II 350.443
Ti II 338.783	Co II 338.817
Ti II 338.376	<u>Cr II 338.268</u>
Ni I 361.939	Fe I 361.876
Ni I 352.454	<u>Co I 352.345</u>
Fe II 276.893	Cr II 276.859
Hg I 280.443	<u>Mg II 280.270</u>
Zn I 330.259	Na I 330.298
Co II 252.897	Si I 252.851
V II 351.730	Co I 351.835

Table 8.2Interference lines among the analytically useful spectral lines detected in PVC and
the sensitive lines of XRF-measured elements in sediment

8.5 Simulated Sediment Matrix Calibration Tests

The ability to achieve unbiased quantitative calibration in the sliding spark strongly depends on the close matching of the matrix used with the real analysis sample, in terms of their thermodynamic properties. Brenner *et al.* [245] observed that time-intensity curves generated by a controlled waveform high-voltage spark were similar to those of dc-arc discharges, suggesting that the matrix ablation process is essentially thermal in character, i.e., the mean time between electron collisions in the plasma is much shorter than the pulse duration of the sparks In sliding sparks, too, thermal processes are primarily responsible for sample ablation and excitation, as was observed in the variable time-intensity profiles reported earlier (see Chapter VII). Since the temperature rise that occurs in the sliding spark may be assumed to be spatially confined to the cylindrical plasma column, with a penetration roughly given by the inverse of the absorption coefficient of the surface layers for the heating wave, the plasma density (in terms of ablated particles per unit volume), which is strongly dependent upon sample composition, is therefore a direct function of the heating processes.

8.51 **Simulated Sediment Analyte Responses**

Simulated sediment, prepared to match as closely as possible the sediment matrix, according to the scheme shown in Table 8.3, deduced from the typical matrix composition of sediment as described earlier (see section 5.1), was used to predict the expected analyte spectral responses in a typical sediment. The objective was to infer the best applicable calibration strategy for quantitative analysis in real sediment. Due to the similarity of the dominant component, quartz, in both matrices (simulated and real sediment), little difference should in principle be expected in the sample ablation characteristics and therefore analyte responses.

Sediment component	Simulate	Fraction in matrix		
Quartz	SiO ₂	62.50 % by weight		
Chlorite + mica Organic carbon	Cellulose	25.00 % by weight		
Inorganic carbon	$(Na_2CO_3)^1$	6.25 % by weight		
Metallic oxides/carbonates	$CaO + K_2CO_3$	6.25 % by weight		

Table 8.3 Formulation of the simulate sediment used in the test analyses

The simulate sediment was diluted with PVC at 3:1 ratio (sediment: PVC, by weight) to be selfbinding and mechanically stable when pellets are prepared for the analyses.

Table 8.4 summarises the general experimental conditions that were used to make the measurements described below. The same experimental conditions were also used to obtain the results shown in Table 8.5, Table 8.6, Table 8.11 and Table 8.12 and Fig. 8.7 and Fig. 8.8.

Table 8.4	Experimental measurements	conditions	used in	n the	test	and	performance	characterisation
Capacitance			14 µl	7				
Discharge cor	ndition		'Hare	l'				
Scan time			500 i	ns				
Scans			10					
Electrode gap			4.5 n	ım				

¹ Mixed with 40 % active charcoal - to prevent using the latter entirely, which would change the conducting properties of the sample matrix

Upon analysis, a substantial drop was noted in the spectral response as reflected in the intensities of selected spectral lines of Y (spiked at 300 ppm in the matrix) between the pure PVC and the simulated sediment (Fig. 8.2a).

A more marked but similar drop is noted in real sediment spiked with the same concentration of Y but containing 2250 mg sediment in 3 g of matrix, i.e., same 3:1 weight proportion of PVC dilution (Fig. 8.2b).

This indicates that although the matrix ablation is similar in both simulated and real sediment, the spectral line signal suppression varies. This may be due to the influence of phase-selective ablation in the real sediments, because the various phases are thermodynamically distinct, moreover they selectively and differentially sorb the heavy elements. Sediment phases are difficult to practically simulate.

It can also be observed (Fig. 8. 2b & Fig. 8c) that a change of matrix composition involving spiking only 25 mg of sediment in 3 g of matrix (i.e., in 2975 mg PVC) causes signal suppression of about 20 % for Y II 377.433 and 85 % for La II 379.478 - spiked also at 300 ppm in the matrix). Thus, external calibration for quantitative analysis of sediments using the sliding spark technique, seems to be only possible when internal standards are used to correct for the phase-determined matrix ablation variations.

The same argument holds concerning the utility of calibration models developed based on one class of sediment (e.g., river sediment) in another sediment (e.g. Sea, Lake, Reservoir, Stream), or between various sediment samples derived from different locations with varying geological characteristics.



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Fig. 8.2 Comparison of matrix influence on spectral response in real and simulate sediment



Fig. 8.3 Selected examples of the elemental spectral responses in simulate sediment

8.52 Simulated Sediment Calibration by SAM

Fig. 8.3 shows selected examples of the sliding spark response functions for the elements Zn, Cd, Ti, Cu, Mn, and Pb in the simulated sediment matrix. Within the indicated confidence limits, the spectral responses can be taken to be representative of those expected in the typical real sediment: the least squares fitting correlation coefficients (viz. 0.9300 - 0.9800) are however poorer than those obtained for the same lines and concentration interval in PVC.

The intensities (and thus the signal-to-noise ratio) are also lower, and some lines that had shown a power law relation in PVC fail altogether to respond similarly in the simulated sediment.

This suggests that for the analytical lines selected for quantitative analysis based on the PVC to be valid in sediment, they must be re-evaluated for direct application in analysis, due to possible spectral interference and decreased precision as a result of lower signal to noise ratio resulting from the general spectral line signal suppression caused by the silicate matrix.

Consequently, all the analytical lines pre-selected for quantitative analysis were re-evaluated in the simulated sediment, using standard addition method calibration.

8.6 Quantitative Analysis Based on Spectral Line Intensity Ratio

8.61 Theoretical Basis

The intensity of a spectral line emitted from the plasma in the pulsed discharge, undergoing a transition $i \rightarrow j$, integrated over the line profile, is given by (see Chapter IV):

$$I_{ij} = h v_{ij} A_{ij} N_o g_i \mu^{-1} \exp\left[\frac{-E_i}{\kappa T_{e^-}}\right]$$
(8.14)

where *h* is Planck's constant, v is the frequency of the transition, *A* is the transition probability, N_o is the ground state analyte particle number density, and *g* and *E* are the statistical weight and energy of the upper level *i*, respectively, μ is the partition function, *k* is the Boltzmann constant, and T_{e} is the electron temperature.

The intensity ratio, therefore, of a spectral line emitted by a trace element (denoted q) in a sample surface layer subjected to sliding spark excitation, to that emitted by some major constituent in the sample can be written as follows:

$$\frac{I_q}{I_p} = \frac{N_q A_q v_q g_q \mu_p}{N_p A_p v_p g_p \mu_q} \exp\left[\frac{\Delta E}{\kappa T_{e^-}}\right]$$
(8.15)

Here, ΔE is the difference between the upper levels of the respective energies. Consequently, in principle, a plot of the intensity ratio against 'fractional' concentration of the trace element should result in a linear relationship.

It is apparent from Eqn. 8.15 that it is desirable to use lines with transitions having as similar upper energies as possible: the intensity ratio in that case depends only weakly on temperature; in the sliding spark this is especially important since the electron temperature has both temporal and spatial dependencies (see Chapter IV).

The results presented in Fig. 8.3 suggest that the efficiency of vaporisation and atomisation in the sliding spark discharge (which is reflected in the quality of the least squares fitting of the calibration curves) depends on the proportion of PVC (matrix modifier) to the surrounding analyte atoms of the sample matrix: the higher the proportion of the matrix modifier, the higher the degree of atomisation.

This is corroborated with the trends observed in Fig. 8.2.

However, the results of Fig. 8.3 nonetheless suggest that quantitative analysis of sediment using the sliding spark technique is possible. The challenge is to improve the precision, sensitivity and quality of the least squares fitting of the analytical models.

They also suggest that the use of an appropriate internal standard to compensate for the interelement effects variations in the simulate sediment may improve the quality of the sediment calibration.

To test the feasibility of internal standardisation to achieve this goal, selected lines of La, Y, C, Cl and Si were used to check their utility to compensate for inter-element effects.

Selected results (for Si and Y) are shown in Fig. 8.4. Depending on the internal standard used, the linear least squares correlation functions range from about 0.980 - 0.997. This indicates that, by carefully choosing the internal standard and line to use in the matrix compensation, real sediments may be analysed to good accuracy by using La, Y and Si as internal standards.

Some performance criteria for selected calibrations are shown in Table 8.5. It may be noted that the quality of the least squares fitting of the spectral response functions based on line ratios are better than those based on the absolute intensities.



Fig. 8.4 Test of performance of internal standardisation in the calibration of simulate sediment

 Table 8.5
 Comparison of some response functions in simulated and real sediment to test the response of internal standardization for selected spectral linesⁱ

Simulated							
Sediment							
Line/nm	SAM response	Maximum	\mathbb{R}^2	SAM response with internal	Internal Standard	Maximum range	\mathbb{R}^2
	function	Range		standard		(ppm)	
		(ppm)					
Zn I 472. 216	y = 0.106x + 13.551	300	0.9344	y = 0.0008x + 0.0125	Y II 488.369	300	0.9964
				y = 0.0005x + 0.0067	Y II 378.870		0.9964
				y = 0.0003x + 0.0046	Y II 377.433		0.9951
Mn II 260.569	y = 0.1888x + 41.388	500	0.9482	y = 0.0017x + 0.2947	Y II 488.369	500	0.9837
				y = 0.0024x + 0.3627	Y II 354.901		0.9931
				y = 0.0002x + 0.0391	Si II 390.533		0.9909
Pb I 368.347	y = 0.1074x + 7.9032	1400	0.9789	y = 0.0014x + 0.1507	Y II 488.369	1400	0.9927
				y = 0.0007x + 0.0843	Y II 378.870		0.9902
				y = 0.0005x + 0.0555	Y II 377.433		0.9902
Rea River							
Sediment							
Line/nm	SAM response	Maximum	\mathbb{R}^2	SAM response with internal	Internal Standard	Maximum range	\mathbb{R}^2
	function	Range		standard		(ppm)	
Zn I 472. 216	y = 0.2178x + 18.20	600	0.9964	y = 0.0009x + 0.0523	Y II 488.369	600	0.9964
				y = 0.0007x + 0.0473	Y II 378.870		0.9951
				y = 0.0004x + 0.0288	Y II 377.433		0.9949
Mn II 260.569	y = 0.4642x + 42.43	500	0.9910	y = 0.0018x + 0.1259	Y II 488.369	500	0.9970
				y = 0.0048x + 0.2795	Y II 354.901		0.9966
				y = 0.0039x + 0.3132	Si II 390.533		0.9935
Pb I 368.347	y = 0.769x + 114.17	700	0.9935	y = 0.0031x + 0.3414	Y II 488.369	700	0.9989
				y = 0.0025x + 0.3011	Y II 378.870		0.9988
				y = 0.0015x + 0.1833	Y II 377.433		0.9981

ⁱy is the instrumental response (intensity or intensity ratio) while x is the concentration of the test standard
The lower sensitivities and precision in simulate sediment are probably due to the inadequate proportion of matrix modifier used to prepare the samples. For the same analytical range the sensitivities for SAM calibration are higher in real sediment than in the simulate sediment. This is probably due to the higher vaporisation (and atomisation) efficiency in the real sediment samples, which was prepared with a higher (75 %) proportion of PVC.

However, the sensitivities are almost the same when SAM calibration is used in conjunction with internal standard. This shows the power of internal standardisation to compensate for wide matrix variations. With proper and careful matrix matching, this result also indicates that, it is possible to simulate sediment and to perform external calibration for real sediment analysis.

8.62 Calibration Utilising Internal Standards

The principle of the use of internal standard i.e., a matrix-based, or added-element whose concentration does not change with changing analyte concentration is derived from Eqn. 8.15. It is a simple concept, but so powerful that it lies at the heart of modern spectrometric analysis; it was even responsible for transforming the spectrographic technique from a qualitative and semiquantitative method into a quantitative method of instrumental chemical analysis. Today, the internal standard method remains central to modern spectrometric analysis, whether the excitation is by arc/spark or by the novel inductively coupled plasma.

In sliding spark spectroscopy, it is even more prudent to employ an internal standard, since the technique is plagued by multiple problems related to quantification, running the gamut from non-uniform ablation to self-absorption in the plasma itself. The most direct advantage of the internal standard method is that the ratio between the signals would be independent of the ablation mass; non-uniform ablation is especially pronounced in inhomogeneous materials or material which exhibit differences in composition, in order to compensate for fluctuations in the ablation process. In analysis samples like sediment, the behaviour of minerals with respect to ablation for instance, varies greatly.

The internal standardisation technique would also be useful to correct for matrix effects and to eliminate the effects caused by the drift in the background and baseline, and the measurement parameter-induced stochastic fluctuations deriving from shot-to-shot spark variations. A further advantage of internal standardisation is that the ratio between the signals is independent of time-dependencies in the signal evolution.

Essentially, internal standardisation as a correction for matrix, and multiplicative effects in general is based on the assumption that the analyte and the element added as in internal standard

undergo an equal relative matrix-induced signal intensity shift. The results reported in this dissertation show this to be the case, to a large extent. However, despite a close match in terms of excitation energies between the analyte and the internal standard, the accuracy of the signal normalisation and hence the results cannot be taken for granted.

The element used as an internal standard would need not only to have an excitation profile in the sliding spark discharge similar to that of the element being analysed; it should have comparable vaporisation and atomisation in the discharge plasma. In essence, for ionic lines, it is not their excitation energies that must match, but the total of the excitation and ionisation energies.

When a calibration curve generated using relative line intensities compares well with that obtained using an internal standard, this may be taken as evidence of complete atomisation of the analytes in the material that has penetrated into the relatively hot centre of the plasma column [246]. When a calibration model generated based on the intensity ratio leads to accurate quantitative predictions, it indicates that, assuming LTE prevails, the plasma composition ratio equals the underlying sample matrix concentration ratio.

In the sliding spark technique this implies that one species of the sample matrix is not vaporised or excited preferentially over the other. The influence of sample matrix effects and the selective volatilisation of some element species are of prime concern in sliding spark analysis.

Long-term drifts may also be corrected by normalising the spectra against the integrated plasma intensity collected by the instrument in the entire investigated spectral range [247].

The improvement in the precision through the use of internal standards is shown in Table 8.6, where sliding spark measurements were made on a sediment sample bound in PVC. The centre column gives the precision of the analytical spectral line alone, while the next column shows the precision of the intensity ratio with respect to the spectral line in parenthesis.

Spectral line	Line intensity	Intensity ratio
~Foorm mo	(% RSD)	(% RSD)
Y II 378.870	7.2	6.4 (with C I 247.856)
La II 492.179	11.6	6.9 (with Cl II 479.454)
Al I 396.152	5.4	5.1 (with Si II 386.251)

|--|

8.7 Quantitative Analysis of Additives in PVC

Fig. 8.5 shows selected working curves obtained by plotting spectral line intensity against the corresponding analyte concentration in PVC. Also shown are calibration curves, for the same spectral lines, derived from data obtained using the internal standardisation method.

As can be noted, use of internal standard leads to significant improvement in the correlation coefficients and linearity of the least squares-fitted response function. The other analytical figures of merit also improve.

It may be concluded that over an extended concentration range (mostly over between 500 - 1000 ppm depending on the element and spectral line), without use of the internal standard, sliding spark relative spectral line responses can only be fitted with non-linear functions.

However, with the use of internal standard the spectral responses are linearized over enhanced concentration ranges thereby extending the analytical utility of sliding spark spectrometry from the trace to the minor concentration regime.

A larger scattering of the data is also observed when internal standard is not used. This means when internal standardisation is used, there are less inter-element (matrix) effects and the calibration improves.

Scan time	200 ms	
Source capacitance	14 µF	
Number of scans	Element-depender	<u>it</u>
	Ti, Fe, Ni	10
	Pb, Hg, Cd	4
	Cr, Mn, V	8
	Cu, Al, Zn, Co	12
Discharge condition	'Hard'	
Number of pre-sparks	1	
Matrix modifier	PVC	
Electrode gap	4.6 mm	

Table 8.7Experimental conditions used for the various calibration model building, trace
quantitative analyses, and validation analysis measurements

The results presented in Fig. 8.5 also indicate that direct quantitative analysis in PVC-based polymer materials may be accomplished by use of sliding spark spectrometry, either by using the standard addition method calibration alone (LHS) or the standard addition method coupled with internal standardisation (RHS). The experimental conditions used for the measurements are shown in Table 8.7; the same conditions were used for all the measurements reported in this chapter, which are not highlighted with respect to the set of conditions shown in Table 8.4.

Fig. 8.5 and Table 8.8 considered together show that internal standardisation improves the dynamic analytical range, the quality of least squares fitted regressions on the spectral response functions, and the elemental detection limits for the generated calibration models.

The data reported in Table 8.9 further indicate that specific trace concentration ranges exist for which the analytical performance of the calibration is optimum: in this range the quality of fitting are enhanced and for most spectral lines, they are almost independent of the calibration strategy used (viz., normal SAM, or SAM in conjunction with internal standardisation).

The clear analytical capability of sliding spark spectroscopy in the reported results is especially important because synthetic PVC-based polymers are widely used in industry, especially as resins. Mostly, certain additives are incorporated into the polymers; these achieve optimum efficiency at trace concentrations as either stabilisers, oxidation inhibitors, fungicides, pigments, platicizers or UV absorbers, among others. The additives could be in the form of organic (e.g., stearates) or inorganic molecules (e.g., oxides). Presently however, there is still a general lack of commercially available certified reference polymer material with trace concentration to test with certainty the accuracy of new methods for PVC analysis.

In Table 8.10, the predicted concentrations of Ti, V, Mn, Cd, Al and Cu, in PVC², based on the generated analytical models and analytical criteria (see Chapter VI), are given.

The analysed elements were chosen so as to be compared with the results of the same elements obtained by the XRF technique. Only these elements (among the elements of interest analysed) were measured by the XRF technique above their detection limits for powder samples.

The *Spectro Xepos* model tube-based XRF spectrometer employing sample irradiation with polarised primary rays was used.

² High molecular, Fluka, FRG



Fig. 8.5 Selected examples of comparative analytical performance of SAM calibration in PVC

Table 8.8Analytical figures of merit for spectral responses of selected lines tested for
various calibration strategies in sliding spark analysis of PVC

Element	Polynomial	Linear	Linearized	Int. Std.	Max.	Linear	LOD with
/line	regression	regression	with Int. Std.	line	dynamic	reg. LOD	Int. Std.
	coefficient	coefficient	regression	used	range	(ppm)	(ppm)
			coefficient		(ppm)		
Ti II				Cl II			
323.452	0.9982	0.9895	0.9948	481.946	3000	4.05	0.97
V II				Cl II			
313.333	0.9979	0.9714	0.9915	481.946	2500	6.86	1.70
Mn II				Cl II			
260.569	0.9971	0.9865	0.9930	481.946	3000	7.32	6.55
Cu II				Cl II			
224.700	0.9928	0.9669	0.9815	481.946	3000	11.85	7.96
Cd II				Si I			
226.502	0.9919	0.8900	0.9906	252.851	1000	7.69	1.36

Table 8.9Analytical figures of merit for spectral responses of selected lines tested for
optimum linear range and calibration strategy in sliding spark analysis of PVC

Element/	Optimum	Max. range for	LOD	LOD after use of	Internal
line	linear range	linear response	(ppm)	Int. Std. at	standard
	regression	regression		optimum range	regression
	coefficient	coefficient		(ppm)	coefficient
Ti II					
323.452	0.9962	1500	1.90	2.30	0.9978
V II					
313.333	0.9920	750	1.70	0.28	0.9964
Mn II					
260.569	0.9908	1500	3.45	3.80	0.9936
Cu II					
224.700	0.9978	300	0.18	0.18	0.9981
Cd II					
226.502	0.9999	400	0.82	0.42	0.9968

Some spectral lines yield more accurate results than others, notwithstanding the sometimes better detection limits of the poorer lines. The sliding spark technique results compare well with those obtained using the XRF technique. Except for Pb, whose concentrations (however) do not differ significantly (SSS³: 7.7 ppm; XRF: 5.0 ppm – see Table 8.10), the average values of concentrations obtained using the sliding spark technique compare excellently with those obtained using the XRF technique, viz., Ti (\pm 2.3 %), V (\pm 0.58 %) and Hg (\pm 5.5 %).

³ Sliding spark spectroscopy

Element (line)	Sliding aparly prediction	LOD	VDE (abcolute amon)
Element (Inte)	Shalling spark prediction	LOD	ARF $(\pm \text{ absolute error})$
	based on SAM calibration	(ppm)	
	(ppm)		
<u><u>Ti</u></u>			
Ti I 498.173	26.5 ± 2.38	0.883	
Ti II 338.783	22.5 ± 2.35	0.750	
Ti II 350.489	34.8 ± 4.18	1.162	$26.0 \pm 1.5 \text{ ppm}$
Ti II 334.188	13.7 ± 2.74	0.456	
Ti I 328.766	14.5 ± 2.92	0.483	
Ti II 323.452	30.8 ± 3.10	1.026	
V			
_			
V II 351.730	55.0 ± 4.95	1.833	
V II 327.112	37.5 ± 3.67	1.233	
V II 313.333	52.1 ± 4.95	1.233	$46.8 \pm 6.0 \text{ ppm}$
V II 311.838	41.5 ± 4.30	1.366	
V II 297.226	37.5 ± 3.10	1.733	
Hg			
Hg II 398.396	7.6 ± 0.78	0.253	
Hg I 280.443	12.2 ± 2.44	0.406	7.2 ± 2.4 ppm
Pb			
Pb I 368.347	7.7 ± 1.08	0.256	$5.0 \pm 1.6 \text{ ppm}$
Al			
Al I 396.152	24.5 ± 2.55	0.817	3.4 ± 0.4 %

Table 8.10Determination of trace element additives in PVC polymer powder using sliding
spark spectroscopy and comparison with the X-ray fluorescence technique

On the other hand the XRF analysis showed that PVC has an Al concentration of 3.4 %. While sliding spark showed 24.5 ppm. This result is deliberately included in Table 8.10 to demonstrate how the use of a calibration model whose maximum dynamic concentration range is exceeded by the concentration of the element of interest in the analysed sample matrix leads to inaccurate quantitative prediction. The maximum dynamic concentration range established for Al working curve in PVC in sliding spark spectroscopy is far below 3.4 %.

The results in Table 8.6 through Table 8.10 prove the power of sliding spark spectroscopy for accurate trace element analysis. The ability to realise this analytical utility depends on the concentration range of interest within the dynamic range, the calibration strategy employed, and the spectral line utilised. In principle, the use of internal standardisation has been shown to possess great potential to reduce the detection limit, increase the analysis precision and to

enhance the concentration range accessible to measurement. It is prudent therefore that more study be directed towards the feasibility of utilising the internal standardisation technique.

8.8 Selection of Internal Standards

The analysis of PVC polymer using the sliding spark technique is less complicated in comparison to the refractory materials. In a complex matrix the choice of internal standard becomes critical in achieving accurate results. First, the emission spectra of the standard must be free from lines of the high concentrations atoms excited in the analysis sample.

Two types of internal standard lines may in principle be used:

- A weak (non-sensitive) spectral line of a major component of the sample matrix.
- A strong (sensitive) line of an element that is not initially present, but is added to the sample.

For sediment, which has been used as a model matrix, the most appropriate element to use for internal standardisation would be Si – especially to compensate for mineralogical effects. Cl and C lines may also be used when the sample is bound in PVC.

But the use of one of the major components in the samples as an internal standard implies knowledge of its concentration; this necessitates - where the concentration is not known - a prior measurement using a different analytical method, e.g., XRF spectroscopy.

The alternative is addition of a known amount of external element to the sample. This alternative is however tedious and prone to spiking errors.

In this work Y (as Y_2O_3), In (as In_2O_3) and La (as La_2O_3) were investigated for use as addedinternal standards to be used routinely in quantitative sliding spark spectroscopy. Since only one line of In was detected that showed a power law relationship between its intensity and the concentration spiked in the matrix as an oxide, only Y and La were chosen.

La and Y have very rich spectra and many lines were excited and measured (Table 8.11). The bolded lines, which are sensitive and linear at trace concentration, were selected. Matrix-component internal standards were also investigated for the elements Cl, C and Si. Interference-free lines from these elements for possible use are shown in Table 8.12.

Element line	λ (nm)	Excitation Energy $E_i(eV)$	Intensity ⁴
Y II	508.743	3.52	75
La II	492.179	2.76	80
Y II	488.369	3.62	160
Y II	485.487	3.54	75
La II	474.873	3.53	28
Y II	412.492	3.41	32
La II	408.672	3.03	550
La II	403.169	3.39	280
La II	398.852	3.51	440
La II	394.910	3.54	900
La II	392.922	3.33	220
La II	391.605	3.40	130
Y II	383.289	3.41	460
Y II	381.834	3.37	150
La II	379.478	3.51	460
La II	379.083	3.39	440
YII	378.870	3.37	850
YII	377.433	3.41	1200
La II	375.908	3.54	280
Y II	371.029	3.52	1500
Y II	366.461	3.56	350
La II	364.541	3.40	120
Y II	363.312	3.41	1000
La II	362.883	3.54	38
YII	362.871	3.54	240
YII	361.105	3.56	1000
YII	358.451	3.56	420
YII	354.901	3.62	500
La III	351.714	5.21	10
Y II	349.608	3.54	220
La II	338.091	3.99	200
La II	333.749	4.12	200
Y II	324.228	4.01	800
Y II	320.332	3.98	280
Y II	317.942	4.00	28
La II	295.050	7.73	12

Table 8.11Spectral Lines excited and identified for use as added internal standards in sliding
spark spectroscopy [215]

⁴ The intensities are assigned on a relative scale in which the most intense line of a given element has 1000 relative intensity units. The relative intensity of the spectra of atoms and ions varies greatly according to the parameters of the power supply of the estimating light source. Thus, the above intensity estimates can only serve for comparison of the lines of one and the same element.

Element line	λ (nm)	Excitation Energy E _i (eV)	Intensity ⁵
Cl II	507.825	18.15	150
Cl II	497.012	18.13	50
Cl II	491.772	18.22	125
Cl II	490.476	18.23	125
Cl II	489.677	18.24	200
Cl II	481.946	15.94	200
Cl II	479.454	15.95	250
Cl II	478.132	19.68	75
Cl II	386.140	19.17	50
Cl II	385.138	19.17	75
Cl II	356.068	26.83	30
Si I	390.553	5.08	11
Si II	386.251	10.06	300
Si III	379.612	24.98	300
Si III	379.141	24.98	250
Si II	318.897	19.30	150
Si III	254.182	15.14	300
Si I	252.851	4.93	200
Si I	251.611	4.95	360
CII	251.206	18.65	600
СІ	247.856	7.68	1000
C IV	240.510	55.78	70
C III	229.687	18.09	1300

Table 8.12The lines identified for use as matrix internal standards in the analysis [215]

Because of matrix and self-absorption effects in the sliding spark plasma, and of the fact that optical thickness is wavelength-dependent, the absolute certainty of the utility of an added-internal standard in sliding spectroscopy could only be obtained by experimental verification.

 $^{^{5}}$ The intensities are assigned on a relative scale in which the most intense line of a given element has 1000 relative intensity units. The relative intensity of the spectra of atoms and ions varies greatly according to the parameters of the power supply of the estimating light source. Thus, the above intensity estimates can only serve for comparison of the lines of one and the same element.

Each selected analytical line was tested against all the spectral lines detected from Y and La. 36 (added) internal standard lines and 23 matrix-based internal standard lines were tested against each analysis line. It was found that not all line pairs of an analyte and matrix are homologous.

It was observed, for instance, that, an ionic line of the matrix element does not couple well with an atomic spectral line. Lines, which also over-fit the data, yielding false positives or artificially lower errors, were found.

For each analysed element, homologous lines, which work together to compensate for changes in the excitation conditions, were tested. The most precise lines were afterwards selected for evaluation of the results. It appears there is no set of necessary and sufficient conditions that exist for assigning homologous lines in sliding spark spectroscopy.

More study in this area is necessary. This can be explained in terms of thermo-physical properties and energy potentials. For any two elements used, homologous however, their excitation potential must be similar, or, in the case of ionic lines, the combined excitation and ionisation energies must be similar. The lines should even be from the same wavelengths region to minimise calibration errors.

Beyond this one must turn to experimentation. Due to a number of factors - for instance, as shown in Chapter IV, different plasma temperatures are computed for the sliding spark plasma, indicating the existence of atomic and ionic populations that are rapidly varying for a given point and time in the plasma development. The neutral species emission occurs primarily in the cooler wings of the plasma and the ionic emission occurs primarily along the axis. Thus in principle, a given pair of homologous lines ought to be selected not only from the same ionisation state but also from the same fixed plasma temperature. In Table 8.6, the values obtained for the intensity ratios should be far better if the lines were homologous.

A more accurate investigation would be a point-to-point comparison at specific plasma times and positions. This would reduce both the temperature and spatial dependence in the plasma, i.e., it would ensure the lines are emitted from the same region of the plume, to also reduce errors due to plasma inhomogeneity. Resonance lines should be avoided, to reduce the possibility of self-absorption (less likely however at trace element concentrations, which are of major interest in this work). In sliding spark spectroscopy, the ionisation (and excitation) probability of every element (and thus spectral line) is critically dependent on the individual physical characteristics of chemical elements such as ionisation potential, cross section of electron impact, melting and boiling temperatures, volatility, etc. It is tedious to choose one suitable internal standard for the correct determination of trace element of analytical interest.

The quality of the calibration models not only depends on the selection of the lines whose ratio is to be used in the analysis, but also on the quantity of the internal standard spiked in the sample. This is shown in Fig. 8.6. In Fig. 8.6b and in Fig. 8.6c, the appropriate concentration regimes to use are marked out for La and Y. It is noted that at particular concentrations of the internal standard in the matrix the response functions plateau out. If such concentrations are utilised, the spectral lines involved would not respond to changes in matrix variations and other effects, which the internal standard is expected to be sensitive to so as to compensate.

In Fig. 8.7 are shown the results of a random test on the utility of the selected internal standards in sediment analysis. The results indicate both the usefulness of carefully choosing the concentration of the internal standard (also implied in Fig. 8.6) and of the emission line to be used; and also that the standardisation technique compensates for matrix effects in sediments containing element concentrations at very low trace concentration.

But the most useful interpretation to be drawn from the data is that SAM calibration based on dilution by the matrix modifier (PVC) may be used in sliding spark analysis of sediment when coupled with the internal standardisation technique. Surprisingly low concentrations of the element present in the sediment have been shown to respond linearly under this calibration strategy.

The masses labelled 1, 2, and 3 in the figure, for the (added) internal standards, correspond to 0.5, 1.0 and 2.0 mg of the oxide. The concentration of the relevant elements contained in the elements used for the tests are given in Table 8.14 (as determined by the XRF technique). Matrix-derived Cl II 507.825 line is also tested as an internal standard; the results indicate that the line effectively, for both Ti and Mn, compensates for the inter-elements effects between the matrix variations in the three matrix types examined.

It is noteworthy that the concentration for the elements V, Cu, Zn for which the responses shown are obtained, are very low. The results shown are therefore an indication of the high sensitivity of sliding spark spectroscopy with use of internal standardisation for quantitative analysis when calibration is based on dilution technique. The curvatures of the responses are indicative of the probable element concentrations in the sediment, which correspond to the detection limits in the matrix.







(b)



(c)

Fig. 8.6 Exploration of 'effective' concentration of La and Y when used as internal standards



Fig. 8.7 Tests of the utility of internal standardisation technique in sliding spark spectroscopy

8.9 External Calibration by Matrix Dilution and Internal Standardisation

The results obtained so far (see section) suggest external calibration is applicable in sediment, with internal standardisation yielding better quality of least squares-fitted analytical models.

Consequently, the calibration was performed using River Rhine (Germany) sediment. The calibration standards were generated by diluting the sediment with PVC in the range 25 mg sediment in 3 g of matrix to a maximum of 2500 mg sediment in 3 g matrix. Each sample pellet was spiked with 300 ppm Y and 320 ppm La, to be used as internal standards.

In principle, although each calibration standard represents increasing element concentration, the matrix at each concentration of the analyte is entirely different (this is unlike in the case of the standard addition method) and the linearity in the spectral response is expected to be diminished with increased concentration by the increasing intensity signal suppression caused by the increased sediment matrix proportion. Optimum and linearized responses, therefore, of the calibration curves are expected only when internal standards are employed.

Fig. 8.8a and Fig. 8.8b show selected calibration curves for some of the elements analysed, plotting both measured intensities and intensity ratios. The correlation coefficients of the least squares-fitted responses for each calibration are indicated inset each graph shown. It is noteworthy that the coefficients are better for the case where the internal standards are used, than for the case where the absolute intensities are used to generated the calibration.

Fig 8.8a shows that under calibration by matrix dilution, relative intensities for some elements yield a power law relationship with the element concentration in the sediment, but the function suffers faster from self-absorption at lower concentrations of the element (i.e., increasing amount sediment in the matrix) so that only polynomial functions can best describe the spectral response function.

This is demonstrated for the cases of Ni I 361.939 and Fe I 271.111 spectral lines. However, the spectral response linearizes due to intensity ratios extend by more than twice the dynamic concentration range defined when absolute intensities are used, over which the calibrations are fitted to better quality as indicated by the correlation coefficients of the least squares fitting, as compared with the fitting on the absolute intensities, which have poorer correlation coefficients in spite of fitting to a non-linear function. Nonetheless in both cases it was observed for all the elements that the dynamic concentration range does did not exceed the concentration that corresponds to 1000 mg sediment in 4 g matrix (this being maximum for the internal standardisation method); but for the case of absolute intensities plotted against element concentration the range is spectral line-dependent.



Fig. 8.8a Examples of working curves from calibration by matrix dilution coupled with internal standardisation technique



Fig. 8.8b Further examples of working curves from calibration by matrix dilution, and matrix dilution coupled with internal standardisation technique

This implies, one, there is a limit in the proportion of the matrix modifier (in this case PVC) for which matrix excitation (vaporisation, atomisation, ionisation and spectral line excitation) is optimum; and two, the utility of the internal standard lines to compensate for matrix, etc, effects in sediment is limited to cases where the sample matrix does to differ so widely in thermophysical properties – in such a case the internal standard technique is non-effective.

During all calibration measurements in the work reported in this dissertation all sediment: PVC weight ratios were selected to fall in the dilution range 33 mg - 1000 mg sediment in 4 g of sample matrix.

8.10 Multivariate Calibration

Although in practical quantitative analysis, calibration curves based on the use of internal standards may be built in the way described according to Eqn. 8.2, this approach has been shown, using LIBS measurements [248], to be valid only for retrieving the concentration of a single species in a well-defined matrix. The procedure is not inappropriate in complex cases, such as multi-elemental analysis or when *a priori* knowledge of the sample i.e., rough matrix composition, is lacking.

One of the advantages of quantitative sliding spark spectroscopy is that the analyses may be carried out by means of more than one spectral line, because of its capability to simultaneously detect multiple spectral signals of the same analyte. Multi-signal calibration utilising multivariate analysis methods is therefore possible. This increases the reliability of the analysis.

Multivariate calibration also alleviates the problems associated with the difficulty of finding wavelength regions where sensitive, linear analyte responses that can be used for univariate calibration are undisturbed. Spectral interference, which arise from incomplete isolation of net analyte signals, can seriously affect the results of calibration analysis, particularly when high concentrations of matrix interfering components are present. In this case, multivariate calibration is superior to calibration, because it utilises the collective power of simultaneous data, and it offers a statistical solution for a number of analytical limitations through both its process of producing data and of the extraction of the information from these data.

The calibration uses multivariate spectral data (in the case of the sliding spark these should be emissions at several wavelengths identified and selected for the quantitative analysis of a given element) to infer concentrations of several analytes, in the analysed samples.

In principal, multivariate calibration methods find the relationship between responses measured in samples (sample data matrix \mathbf{X}) and vector of concentrations of analyte of interest (\mathbf{y} vector – see Fig. 8.9), in order to predict concentration in a new sample.

The relationship may be linear or non-linear. As a result, analytical models are necessary, the best way to create them being measuring sliding spark spectra of known samples (the training set) and empirically relating the spectra metric to known property (in this case analyte concentration).



Fig. 8.9 Schematic representation of multivariate calibration procedure

8.101 Multivariate Methods

8.102 Inverse and Classical Least Squares

In order to generate a model that will allow predictions to be made at some appropriate level of certainty, there are two possible approaches to calibration modelling, regressing Y on X or X on Y.

In the linear additive model for multivariate calibration (total or classical calibration model) the instrumental responses are modelled as a function of analyte concentration.

In partial calibration (inverse model) the concentrations are modelled as a function of instrumental responses [249].

The process is normally achieved by building a model with data from known samples and then applying the model to the determination or prediction of new 'unknown' samples. The forward prediction (i.e., regressing of Y on X) can be written thus,

$$Y = XB + E \tag{8.16}$$

Typically X would represent the spectra, Y the concentrations of the analyte(s), B the regression coefficients and E the residual error (i.e. noise, etc.). It is then possible to write an equation for prediction, \hat{y}_i for new samples from \hat{x}_i (i.e., spectra) as

$$y'_{i} = x'_{i} (X'X)^{-1} X'Y$$
(8.17)

This procedure is termed 'inverse' calibration, and is commonly referred to as Multi Linear Regression (MLR). One disadvantage of this method is that the analysis has to be restricted to a small number of wavelengths, to ease matrix inversion, which is impossible if the number of dimensions (wavelengths) exceeds the number of calibration mixtures.

In spectroscopy, the model should actually be reversed, i.e., regressing X on Y, as spectra are generated by the analytes – the so-called reverse or K-matrix approach. The reverse model may be expressed as:

$$X = YK' + E \tag{8.18}$$

where X represents the spectra, Y the concentration(s) of the analytes(s), K the matrix of unit spectra, and E corresponds to the residuals. Thus,

$$\widehat{K} = X \, Y (Y Y)^{-1} \tag{8.19}$$

and so the new predictor can be written as:

$$y'_{i} = x'_{i} \widehat{K} (\widehat{K}' \widehat{K})^{-1}$$
(8.20)

This is normally referred to as the classical calibration approach. Classical Least Squares (CLS) and Inverse Least Squares (ILS) are sometimes referred to as P- and K-matrix methods respectively, due to these slightly different mathematical approaches involved.

In whichever case, the main purpose of the calibration is the prediction, the least squares solution for the vector of unknown component concentration, y_i where x_i is the spectrum of the unknown sample.

However this method only works with relatively simple problems, particularly to be encountered in UV/VIS spectroscopy. The approach is limited when the system under study is undetermined, i.e., when there are more components contributing to the spectra than are fully known about.

This is the analytical challenge when utilising analytical spectral information deduced on the basis of a PVC matrix, for applied analysis in more complex matrices such as sediment; or even between the various types of sediment.

Multi-component analysis can be based on different mathematical approaches. Mainly the inverse calibration model is applied (regressing concentrations on responses). The difference between the multivariate regression methods simply lies in the various ways of inverting the response matrix.

Linear as well as non-linear methods are used to estimate the calibration parameters. Typical linear methods are Principal Component Analysis (PCR) or Partial Least Squares (PLS). The non-linear methods can be statistical in nature, i.e., non-parametric regression methods (e.g., Alternating Conditional Expectations (ACE), Multivariate Adaptive Regression Splines (MARS), or they can be based on neural networks computation.

Table 8.11 summarises the important mathematical methods for multivariate calibration. The regression methods commonly applied in analytical spectroscopy, and their fundamental principles and mathematical backgrounds, are discussed in detail in the literature, e.g. [250].

Non-linear non- parametric Regression methods	Neural networks
Alternating Conditional Expectations (ACE)	Back-propagation (BP)
Non-linear partial least Squares (NPLS)	Counter-propagation
Multivariate Adaptive Regression Splines (MARS)	
	Non-linear non- parametric <u>Regression methods</u> Alternating Conditional Expectations (ACE) Non-linear partial least Squares (NPLS) Multivariate Adaptive Regression Splines (MARS)

Table 8.13	The commonl	y used	mathematical	methods	for	inverse	calibration	in	multi-
	component ana	lysis [2	48-251]						

8.103 Linear Methods

The simplest method for multivariate calibration is MLR. MLR assumes that the best approach to estimating concentrations (Y) from responses (X) is to find the linear combination of the variables in X that minimises the errors in reproducing Y. In this method, the matrix of responses X and vector of analytes concentrations y are related as follows:

$$y = bX + E \tag{8.21}$$

where **b**, is a vector of regression coefficients. Eqn. 8.21 can be solved by linear algebra; for example using Inverse Least Squares (ILS) regression, the well-known least-squares solution can be used to obtain,

$$b = (X^T X)^{-1} X^T y$$
(8.22)

where $(X^T X)^{-1} X^T$ is the pseudo-inverse of the response matrix (X) measured for samples with known concentrations of analyte (y), which may be calculated using, for example, the Singular Value Decomposition (SVD) method [252].

Once the regression coefficients b are estimated, concentration of unknown samples may be calculated as follows:

$$y_{new} = bX_{new} \tag{8.23}$$

This solution is possible only for **X** with n > p (see Fig. 8.9). If the condition is not fulfilled, the matrix is singular and the inverse of the product ($\mathbf{X}^{T}\mathbf{X}$) cannot be calculated. In the general case of sliding spark spectroscopy data are correlated, so multiple linear regression involving inversion of matrices, will result in almost a singular matrix, with solutions that are statistically unstable.

There are also other causes, besides analyte-analyte interactions, that lead to not well-behaved systems, such as non-linear responses, nearly optically thick plasmas, line self-reversal, signal interference, high noise, and non-colliniarities. Techniques such as Ridge regression and stepwise multiple regression [253] may be used to solve this problem, because they lead to less correlation among the variables.

Otherwise PCR or PLS are routinely used. Both are multivariate projection full spectrum methods; they are related to each other, and to other multivariate calibration methods such as

CLS and ILS. In fact PLS is composed of a series of simplified CLS and ILS. The ILS method assumes that concentration is a function of emission.

Although these two methods (PCR and PLS) are very useful in the partial calibration context they will not improve the Ordinary Least Squares (OLS) solution to the total calibration if the concentrations are well designed.

The first one, PCR, consists of two steps. One, the original variables are replaced by more descriptive latent variables (PCs – principal components) obtained by Principal Component Analysis (PCA). PCA is a well-known statistical technique for analysing large multi-dimensional data sets. It identifies the directions of the largest variations in the data via the principal components $(\vec{P}_1, \vec{P}_{n,....})$ called scores (new sets of un-correlated variables) and represents the data in the co-ordinate system defined by the PCs. Typically, the number of coherent changes in large data sets is significantly smaller than the original variables and thus PCA provides a representation of the data in the lower-dimensional space of significant variables plus noise, with minimum loss of information. In effect, under PCA the data set of measured values is decomposed into orthogonal matrices of latent variables **L** and corresponding scores **A** and in addition, into a matrix of residues **E** [224].

$$Y = A_{\nu}L^{A}_{\nu} + E_{\nu} \tag{8.24}$$

Eqn 8.24 highlights the dominant patterns and trends in a data matrix **X** in terms of a limited number (A) of latent variables. The scores (columns of **A**) are mathematically orthogonal to one another and constitute an optimal summary of the systematic variation between the observations (instrumental responses). The contribution of the variables (process signals) to the scores are seen in the loadings (columns of **L**). The matrix \mathbf{E}_{y} contains the model residuals. In the second step (of the PCR) MLR is performed on the new variables.

On the other hand the PLS model is based on similar principles as PCR, i.e., projections of original data to latent structures. In fact PLS is the regression extension of PCA. The PLS algorithm however finds simultaneously important and related components of \mathbf{X} and of \mathbf{y} .

PLS has been shown to be a good alternative to classical explicit modelling in spectrochemical analysis because it deals with the colinearity problem and discards noise while retaining analytical information. More detailed mathematical techniques for PLS in relation to other multivariate regression methods are given in, among other works, by Geladi and Kowalski [254], and by Lorber *et al.* [255]. The matrix of independent variables (concentration) is decomposed in the same way as in PCR:

$$X = A_x L_x + E_x \tag{8.25}$$

which has two objectives, namely to well approximate X and Y and to model the relationship between them. The variation in the predictor block (X) is summarised by the X scores A, and the corresponding variation in the response block (Y) is described by the Y scores, D. Basically PLS maximises the covariance between A and D.

For each model dimension a weight vector \mathbf{w} is computed which reflects the contribution of each X variable to the modelling of Y in that particular model dimension. The resulting Y weight matrix W is important since it reflects the structure in \mathbf{X} that minimises the covariance between \mathbf{A} and \mathbf{D} .

The set of PLS regression coefficients, carried out in the space of latent variables, can then be computed according to:

$$L_{y} = DL_{x} + E_{L} \tag{8.26}$$

Because the PCs are orthogonal, there is no colinearity problem.

Robust multivariate statistical methods (e.g., least squared median method) and /genetic calibration, which are insensitive to, and can reduce the influence of outliers, may also be utilised to address spectral non-linearity and colinearity. Besides, they perform a direct estimation of the multivariate detection limits [252; 256-260].

8.11 Validation Tests

The accuracy of the resulting analytical model is tested by a second set of known samples (validation set) and by a statistical analysis of how well the analytical model fits the training set data. The analytical model is also examined for how robust it is likely to be against expected variation in future samples.

Uncertainty in predicted concentration can (assuming all error is normally distributed random noise in the y variable) be estimated by the standard deviation in the sensitivity (slope) and intercept in the least squares fitting approximation.

Elem.	Matrix	Matrix dilution	Best performance internal standard lines
(line)	dilution	calibration (with	
	calibration	internal standard)	
Ti	Ti II 338.376	Ti II 338.376	Y II 488.369; Y II 485.487; Y II 366.461
	Ti II 498.173	Ti II 498.173	Y II 488.369; Y II 378.870; Y II 377.433
	Ti II 350.489	Ti II 350.489	Y II 361.105; Y II 354.901; Y II 363.312
	Ti II 334.188	Ti II 334.188	Y II 354.901; Y II 363.312; Y II 361.105
Zn	Zn I 472.216	Zn I 472.216	Y II 354.901
	Zn I 330.259	Zn I 334.502	Y II 378.870; Y II 354.901
		Zn I 330.259	Y II 354.901
Pb		Pb I 368.348	Y II 488.369; Y II 377.433;Y II 361.105
Ni	Ni I 361.939	Ni I 361.939	Y II 488.369; Y II 378.870; Y II 366.461
		Ni I 352.454	Y II 488.369; Y II 378.870; Y II 366.461
		Ni I 310.771	Y II 488.369; Y II 378.870; Y II 354.901
Mn	Mn II 257.610	Mn II 260.569	Y II 488.369; Y II 378.870; Y II 366.461
		Mn II 257.610	Y II 488.369; Y II 378.870; Y II 366.461
		Mn II 348.291	Y II 488.369; Y II 378.870
Co		Co I 350.228	Y II 377.433; Y II 366.461; La II 295.050
		Co I 345.351	Y II 366.461; Y II 363.312; La II 295.050
		Co II 236.379	Y II 354.901
		Co II 230.786	Y II 362.883; Y II 354.901
V	V II 297.226	VII 297.226	Y II 488.369; Y II 378.870; Y II 354.901
		V II 313.333	Y II 488.369; Y II 378.870; Y II 354.901
		V II 312.528	Y II 488.369; Y II 378.870; Y II 354.901
		V II 311.838	Y II 488.369; Y II 378.870; Y II 354.901
		V II 310.937	Y II 488.369; Y II 378.870; Y II 354.901
Cu		Cu II 221.810	Y II 363.312; La II 295.050
		Cu II 219.226	Y II 377.433; Y II 366.461; La II 295.050
Cr		Cr I 357.868	La II 408.672; Y II 366.461; Y II 362.883
		Cr II 267.879	Y II 488.369; La II 408.672; Y II 378.870
Al	Al I 396.152	Al I 396.152	La II 408.672; La II 364.541; La II 295.050
Cd		Cd I 228.802	Y II 488.369; Y II 377.433; Y II 354.901
		Cd II 226.502	Y II 488.369; Y II 377.433; Y II 354.901
		Cd II 214.441	Y II 488.369; Y II 377.433; Y II 354.901
Hg	Hg I 280.443	Hg II 398.396	Y II 377.433; Y II 366.461
		Hg I 280.443	Y II 377.433; Y II 366.461; Y II 354.901
Fe	Fe II 276.893	Fe II 276.893	Y II 488.369; Y II 378.870; Y II 366.461
	Fe I 274.111	Fe I 274.111	Y II 488.369; Y II 378.870; Y II 377.433

Table 8.14Best spectral lines identified for multivariate sliding spark spectrometric analysis
of sediment utilising matrix dilution calibration with internal standards

It can also be estimated by the root mean square error of prediction, RMSEP, expressed as

$$RMSEP = \frac{\sqrt{\sum_{i=1}^{n} (c_i - c_i)^2}}{n}$$

(8.27)

where c_i is the calculated concentration, c_i is the true analyte concentration and *n* is the number of samples. RMSEP can also be used to identify potential outliers in the calibration.

8.12 Estimation of the Limits of Detection

In order to have a characteristic quantity that can be used to compare the power of the sliding spark technique for any given element analysed in a given matrix, relative to other methods (or to compare the technique for the different elements), detection limits were computed. The detection limit (LOD), which is in itself instrument-, method-, matrix- and element/line-dependent, is an important figure of merit in spectrochemical analysis.

LOD is normally estimated on the basis of the signal-to-background ratio (SBR) of the measured analyte signals and the relative standard deviation of the background signal (RSD_B), commonly by the linear extrapolation from the slope to 3X the standard deviation of the blank signal. The blank value should be identical to the samples except that the analyte is absent, or in such a minute quantity that it will give signals not higher than the background [261,262]. The concept of LOD is discussed in detail elsewhere [263].

The background equivalent concentration (BEC) concept is more appropriate to use in computing LOD in sliding spark spectroscopy. BEC is the analyte concentration, which is responsible for producing a net response signal equal to the background intensity at the analytical line; that is, the analyte concentration for which the SBR equals 1 [264]. The background is essentially the noise in a measurement when no signal is present. The signal-to-background ratio (SBR) may therefore be defined as the signal above background, that is, the net analyte signal ($I - I_B$), divided by the intensity of the background (I_B):

$$SBR = (I - I_B) / I_B \tag{8.28}$$

Usually the noise is determined by statistical fluctuations of the response signal (Fig. 8.12). The standard deviation is a measure of this noise, for which reason the signal-to-noise ratio (S/N) is defined as the mean signal (I) divided by the standard deviation (σ):

$$S/N \simeq I/\sigma$$
 (8.29)

The concept of background equivalent concentration (BEC) is graphically shown in Fig. 8.10. The point 2B corresponds to a signal-to-background ratio of 1. When the BEC is not available, it may be calculated from the following formula, easily derived from Fig. 8.11.

$$BEC = [(C_H - C_L)/I_H - I_L)](I_L - DC) - C_L$$
(8.30)

or

$$BEC = (\Delta C / \Delta I)(I_I - DC) - C_I$$
(8.31)

where $\Delta C = C_H - C_L$ is the difference in concentration between the high (*H*) and low (*L*) calibration standards, $\Delta I = I_H - I_L$ is the difference in the measured line responses (intensity or intensity ratio) of these high and low standards, and *DC* is the dark current.



Fig. 8.10 Schematic sketch showing intensity verses wavelength relationship of the signal to the background



Fig. 8.11 Calibration plot of concentration verses analyte signal intensity

When the low standard is chosen as the blank ($C_L = 0$) then $I_L = I_B$, the background intensity. The dark current may be assumed to be negligible with respect to the background i.e., $DC \ll I_B$, so that Eqn. 8.31 reduces to:

$$BEC = (C_H \times I_B) / (I_H - I_B)$$
(8.32)

where I_B is the background intensity. Eqn. 8.32 simplifies the relationship between BEC and SBR; according to Eqn. 8.28, the term $(I_B)/(I_H - I_B)$ is just the inverse of SBR, therefore,

$$BEC = C_H / SBR \tag{8.33}$$

Since $\Delta C / \Delta I$ is simply the sensitivity, S_i , of the calibration curve, according to Eqn. 8.31,

$$BEC = s_i (I_L - DC) - C_L \tag{8.34}$$

Similarly, in the approximation $C_L = 0$, so that $I_L = I_B$, and $DC \ll I_B$, one finds

$$BEC = S_i I_B \tag{8.35}$$

In spectrochemical analysis, it is taken that the smallest amount of analyte detectable is three times the normal, random, statistical fluctuations of the noise or spectral background (the three standard deviations ensure that any signal is above the noise), i.e.,

$$LOD = 3\sigma_B \tag{8.36}$$

where σ_B is the standard deviation of the blank or pure. But LOD must of necessity be expressed not in terns of units of intensity but in terms of concentration, so in quantitative analysis based on working curves, an accurate calibration for the element must be available in order to estimate the LOD. In ICP this problem is normally overcome by multiplying Eqn. 8.36 with the sensitivity of the calibration curve. In principle, this (short-cut) approach is only appropriate if the calibration curve passes through the origin.

Several measurements on a blank were taken and the average found. The standard deviation and relative standard deviation (RSD) of the intensity signal were also found – in intensity units. The blank standard deviation was taken from 10 measurements of the blank signal determined at the respective spectral line wavelengths. For measurements developing a calibration strategy for quantitative analysis of PVC-based polymers, the blank was PVC powder which had also been subjected to mixing with a ceramic ball mill under similar conditions to those used to prepare the

calibration standards. The signals were background-corrected by the analysis software accordingly as described elsewhere in this dissertation.

For sediment analysis using the standard addition method, simulated sediment mixed in the PVC in the same proportion as was utilised for real sediment was used as a blank. In the external calibration (by dilution of sediment) method based on a series of diluted sediment (with PVC) no clear criterion for identifying the blank was possible; the method of estimating LOD based on the BEC was thus found to be very useful. In terms of the RSD (i.e., standard deviation divided by the mean times 100), the standard deviation of the blank (indicated by the subscript B) is given by

$$\sigma_{\rm B} = (RSD_{\rm B} \times Mean/100) \tag{8.37}$$

Substitution of Eqn. 8.37 into the definition of LOD above (Eqn. 8.38) gives

$$LOD = (3 \times (RSD_B \times Mean)/100)$$
 (8.38)

But the LOD can only be expressed in terms of concentration units. Since it is the blank sample that is being measured in this case, the signal is just the background with a corresponding concentration that is simply the BEC, thus:

$$LOD = (3RSD_{B}.BEC)/100 = BEC/33 \simeq BEC/30$$
 (8.39)

8.121 Analyte Detection Limits in Sediments

Table 8.15 summarises the sliding spark spectroscopy detection limits in sediments obtained for the 11 elements successfully analysed out of the 14 elements studied. The bolded values indicate that the analytical model used gives accurate quantitative predictions.

The detection limits are in general excellent in comparison with other solid-state analysis methods. The ionic lines were observed to have lower (better) detection limits than atomic lines; where exceptions exist it may probably be due to the existence of low background continuum in the region of the spectral line analysed, while the intensity of the line is high.

Element (line)	Sliding spark	LOD for best Internal Standard
	LOD (ppm)	line (ppm)
Ti	••	Si I 252.851
Ti II 323.452	109	45.2
Zn		La II 351.714
Zn I 472.216	44.5	3.30
Pb		La II 351.714
Pb I 368.347	22.6	6.07
Ni		Cl II 479.454
Ni I 352.454	1.8	0.17
Со		La II 492.179
Co I 350.228	9.6	0.40
V		Cl II 481.946
V II 313.333	8	2.66
Cu		Cl II 481.946
Cu II 224.700	3.2	2.13
Cr		La II 364.541
Cr II 336.804	4.4	4.50
Cd		C I 247.856
Cd II 226.502	0.5	0.08
Fe		Cl II 481.946
Fe II 276.893	85.6	46
Mn		Y II 354.901
Mn II 260.569	22.1	13

Table 8.15 Typical limits of detection for sediment in sliding spark spectroscopy

8.13 Calibration Validation and Accuracy Tests

8.131 Analysis of River Rhine Sediment

Generally, the accuracy of any analytical technique is defined by the percentage differences between the experimental and actual values. Another way to assess accuracy is to calculate the residual error between the true, and the values obtained from the calibration curve.

Calibration models were developed for the quantitative analysis of sediment both using the standard addition method coupled with internal standardisation. Examples of the working curves are shown in Fig. 8.12. The analytical models were tested for their power to predict the element concentrations in the River Rhine sediment that had been employed in developing them: Table 8.16 shows the results obtained, together with a summary of the spectral lines used, calibration method utilised, internal standard lines used where applicable, and a comparison with results of the same sample analysed using the XRF spectroscopy technique.

Element/line	SAM	SAM	Internal standard	XRF conc.	Relative
	calibration	(internal	line utilised	(ppm)	sensitivity
	conc.	standard)			coefficient
Ti II 323.452	3512				
Ti I 498.173	3808			3940	1.034
Zn I 472.216		99	La II 351.714	73	1.356
Pb I 368.347		182	La II 351.714	90	2.020
Ni I 352.454	56	52.8	La II 351.714	55	
		78.4	Cl II 481.946		0.960
		44.0	C I 247.856		
Co I 350.228		12	La II 492.179	16	0.750
VII 313.333		80	Cl II 481.946	85	0.941
Cr II 313.205	155	152	Y II 378.870	130	
		113	Y II 377.433		1.069
		139	Y II 362.871		
Cr II 336.804	133	137	La II 364.541		
		148	Si II 386.251		
		96	C I 247.856		1.053
Cd II 226.502		2.4	C I 247.856	2	
		4.8	Cl II 479.454		1.200
Mn II 257.610		976	La II 295.050	880	
		1104	La II 492.179		1.109
		1040	La II 398.852		
Mn II 260.569		928	Y II 354.901		
		1104	Y II 488.672		
		672	La II 492.179		1.054
Cu II 224.700	96	64	Cl II 481.946	80	
		112	Cl II 479.454		0.800
		112	C I 247.856		

Table 8.16Analysis of River Rhine sediment for heavy elements using the developed sliding
spark spectroscopy calibration models and comparison with XRF

The relative sensitivity coefficients (RSC), i.e., measured value/certified value, of analysed elements in the sediments are also given for all the analysed elements. RSC is an important characteristic of elemental analysis.

The results are shown for selected elements, for multiple lines, which indicates the power of multi-signal calibration, to enhance the accuracy of analysis. As depicted in Fig. 8.13, the results obtained are very good for a new analytical method.



Fig. 8.12 Examples of SAM analytical models for the sliding spark analysis of sediment matrix



Fig. 8.13 Comparison between the performance of sliding spark spectroscopy against the XRF method, in predicting the concentrations of heavy elements in sediment

In Table 8.17 are listed the best (in terms of quality of fitting, accuracy) internal standard lines selected for the analysis of trace elements in sediment using SAM calibration. (y is the instrumental response (intensity or intensity ratio) and x is the concentration of the calibration standards. The data are given for only one line for each element, the optimum line to utilise in univariate analysis of the given element using the sliding spark technique.

Table 8.18 shows a summary of the best spectral lines for quantitative analysis of heavy elements in sediment by sliding spark spectroscopy. Those that predict accurate ($\pm < 10$ %) results are marked by (+); those that predict approximate ($\pm 10 \le 15$ %) are marked by (~).

Elem.	Line/nm	SAM calibration	R^2	SAM with int. std.	Int. std.	\mathbf{R}^2
		function		function	line	
Ti	Ti II					
	323.452	y = 0.0904x + 19.843	0.9876			
Zn	Zn I				La II	
	472.216			y = 0.0037x + 0.0231	351.714	0.9951
Pb	Pb I				La II	
	368.347			y = 0.0146x + 0.1662	351.714	0.9980
Ni	Ni I				Cl II	
	352.454	y = 0.5023x + 1.7665	0.9979	y = 0.0003x + 0.001	479.454	0.9939
Co	Co I				La II	
	350.228			y = 0.0036x + 0.0027	492.179	0.9956
V	V II				Cl II	
	313.333			y = 0.0006x + 0.003	481.946	0.9916
Cu	Cu II				Cl II	
	224.700	y = 0.7194x + 4.3524	0.9945	y = 0.0005x + 0.002	481.946	0.9974
Cr	Cr II				La II	
	336.804	y = 0.6027x + 4.9978	0.9952	y = 0.0064x + 0.0555	354.901	0.9966
Cd	Cd II				CI	
	226.502			y = 2E - 5x + 3E - 6	247.856	0.9832
Mn	Mn II				La II	
	260.569			y = 0.0048x + 0.2795	354.901	0.9966

Table 8.17Best calibration models for quantitative analysis of heavy elements in (River)
sediment using the SAM and/ internal standardisation calibration

8.132 Analysis of Certified Reference Materials

The accuracy of the results obtained with the calibration strategies that were developed based on River sediment was investigated using Stream sediment certified reference materials GB-W7311, GB-W7306, GBW-7305, GBW-7307 and SARM-46.

The measured and certified concentrations are presented in Tables 8.19a - e. The various calibration strategies employed for every element in the analyses are also indicated.

The results of the elements are in good agreement with the certified results in view of the fact that the analytical models have been developed using a river sediment and they were tested on stream sediment from different geographical (and therefore geological settings), with varying ranges of the element of analytical interest.

Element (lines)	Standard addition method	Standard addition method
		coupled with internal standard
Ti I 498.173	(+)	
Ti II 337.279	(~)	
Ti II 328.766	(~)	
Ti II 323.452	(+)	
Pb I 368.348		(~) La II 351.714
Ni I 352.901	(+)	(+) La II 351.714
		(~) Cl II 481.946
		(+) C I 247.856
Mn II 260.569	(~)	(~) Y II 488.369
		(+) Y II 354.901
		(~) La II 492.179
Mn II 257.61		(+) La II 295.050
		(~) La II 492.179
		(+) La 398.852
Co I 350.228		(+) La II 492.179
		(~) La II 398.852
V II 313.333		(+) Cl II 481.946
		(~) Cl II 479.454
Cu II 224.700	(+)	(+) Y II 488.369
		(+) Cl II 481.946
		(+) Cl II 479.454
		(+) C I 247.856
Cr II 313.205	(+)	(+)Y II 378.870
		(+) Y II 362.871
		(~) Y II 366.461
Cr II 336.804	(+)	(~) Si I 390.533
		(+) La II 364.541
		(+) Si II 386.251
		(~) C I 247.856
Cd II 226.502	(~)	(+) C I 247.856

Table 8.18The best spectral lines for quantitative analysis of heavy elements in a (river)
sediment matrix by sliding spark spectroscopy

Element/line	SAM calibration	SAM with	Internal Standard	External	External	Internal Standard	Certified
		Internal S	line used	calibration	calibration with	line used	concentration
					internal Standard		(ppm) or (%)
Ti II 323.452	4010±685						
Ti I 498.173	3356±573						4640±180
Zn I 472.216							
Zn I 334.502					70.3±10.5	Y II 488.369	144±10
Pb							27±5
Ni I 352.454	52.2 ±5.0						
							78±7
Ni I 310.771					80.9±9.5	Y II 378.870	
					86.7±8.5	Y II 377.433	
Co II 236.379					30.3±4.6	Y II 354.901	24.4±3.0
V II 297.226							142.12
					59.9±8.4	Y II 378.870	
Cr I 357.869							190±24
Cd II 226.502					1.63±0.4	Y II 488.369	0.43±0.04
Fe II 274.111	(3.2 ±0.43) %	(3.7±0.57) %		(4.8 ±0.41) %			(4.1±0.07) %
Mn II 260.569	1053±97	1318±131	Y II 488.369				970±60
Cu							383±18
Al I 396.152				(5.3±0.78) %			(7.49±0.07) %

Table 8.19aMethod Validation for sliding spark spectroscopy by transfer of the developed analytical calibration models for the analysis of some heavy elements in certified
reference material GBW-7306 (Chinese Stream Sediment)
Table 8.19bMethod Validation for sliding spark spectroscopy by transfer of the developed analytical calibration models for the analysis of some
heavy elements in certified reference material GBW-7305 (Chinese Stream Sediment)

Element/line	SAM calibration	SAM with	Internal Standard	External	External	Internal Standard	Certified
		Internal S	line used	calibration	calibration with	line used	concentration
					internal Standard		(ppm) or (%)
Ti II 323.452							
Ti I 498.173							5370±250
Zn I 472.216	279±51						243±23
Pb							112±13
Ni							34±5
Co II 230.786					18.8±3.8	Y II 354.901	18.9±3.2
					13.5±3.5	Y II 362.883	
V II 297.226					121.1±9.8	Y II 488.369	109±9
					129.6±11.2	Y II 378.870	
Cr I 357.869	59±7.2				55.4±6.0	La II 408.672	70±9
Cd II 226.502					2.89±0.56	Y II 488.369	0.82±0.07
					2.55±±0.38	Y II 377.433	
Fe II 274.111				(4.37 ±0.48) %			(4.08±0.09) %
Mn II 257.610		1075±130	Y II 366.461				1160±60
Cu							137±10
Al I 396.152				(6.73±0.61) %	(5.38±0.25) %		(4.98±0.02) %

Table 8.19cMethod Validation for sliding spark spectroscopy by transfer of the developed analytical calibration models for the analysis of some
heavy elements in certified reference material GBW-7305 (Chinese Stream Sediment)

Element/line	SAM calibration	SAM with Internal S	Internal Standard line used	External calibration	External calibration with	Internal Standard line used	Certified concentration
T: 11 000 450					Internal Standard		(ppm) or (%)
Ti II 323.452	5039±640						
Ti I 498.173	4908±490						4480±180
Zn							238±19
Pb							350±26
Ni I 310.771					78.3±10.9	Y II 488.369	53±5
					85.7±11.4	Y II 378.870	
Со							21±3
V II 297.226					75.3±6.4	Y II 488.369	96±9
					98.2±8.3	Y II 378.870	
Cr							122±10
Cd II 226.502					1.47±0.18	Y II 377.433	1.05 ± 0.08
Fe II 274.111	(4.60±0.30) %	(5.99±0.87) %	Cl II 481.946				(4.55±0.09) %
Mn							690±50
Cu							38±2
Al I 396.152				(4.52±0.59) %			(3.94±0.03) %

Table 8.19dMethod Validation for sliding spark spectroscopy by transfer of the developed analytical calibration models for the analysis of some
heavy elements in certified reference material SARM-46 (South African Stream Sediment)

Element/line	SAM calibration	SAM with	Internal Standard	External	External	Internal Standard	Certified
		Internal S	line used	calibration	calibration with	line used	concentration
					internal Standard		(ppm) or (%)
Ti							
							3354
Zn I 472.216	6009±414						5900
Pb							13000
Ni I 310.771					163±16	Y II 488.369	125
Co II 236.379					57.4±5.6	Y II 354.901	56
V II 313.333				229±17			225
Cr II 313.205	409±69	631±107	Y II 362.871				559
Fe II 274.111					(19.66±0.60) %	Y II 488.369	(19.68) %
Mn II 260.569	9567±747	7760±690	Y II 354.901				8830
Mn II 257.610					8899±611	Y II 366.461	
					8972±741	Y II 488.369	
					7679±760	Y II 408.672	
Cu II 221.810					558±52	La II 295.050	566
Al I 396.152				(6.22±0.22) %	(6.29±0.13) %	La II 408.672	(5.28) %

Element/line	SAM calibration	SAM with	Internal Standard	External	External	Internal Standard	Certified
		Internal S	line used	calibration	calibration with	line used	concentration
					internal Standard		(ppm) or (%)
Ti II 323.452	2124±203						
Ti II 498.173	1804±173						2100±150
Zn I 472.216	279±78						373±21
Pb I 368.347		615±71	La II 351.714				636±34
Ni I 352.454					15.5±2.6	Y II 378.870	14.3±1.5
					16.9±3.2	Y II 377.433	
Co II 230.786					10.14±1.80	Y II 354.901	8.5±1.2
					6.19±2.5	Y II 362.883	
V II 297.226					47.7±5.5	Y II 488.369	47±5
					64.0±7.4	Y II 378.870	
Cr I 357.869	59±7						40±4
Cd II 226.502					3.2±0.9	Y II 488.369	2.3±0.2
					1.5±0.3	Y II 377.433	
Cd II 214.441					2.2±0.2	Y II 488.369	
					1.7±0.5	Y II 377.433	
Fe II 276.893	(3.53 ±0.30) %						(3.07±) %
Mn II 260.569		2807±131	Y II 354.901				2940±130
Mn II 257.610		3481±170	La II 295.050				
Cu II 219.226					102±10	La II 362.883	79±4
Al I 396.152				(5.4±0.59) %			(5.49±0.05) %

Table 8.19eMethod Validation for sliding spark spectroscopy by transfer of the developed analytical calibration models for the analysis of some
heavy elements in certified reference material GBW-7311 Chinese Stream Sediment)

8.14 Discussion

Although the results of the validation analyses shown above yield good results for some elements, at the same time it is difficult to generalise the reasons for why some elements yielded poor results in some matrices.

However, generally, the processes and matrix effects that lead to spectral overlap and line interference, not to mention variations in the basic spectral response, are numerous and vary from sample matrix to sample matrix.

In the sliding spark, for instance, radial velocity of the atoms in the plasma alone produces Doppler shifts on the order of 0.01 nm in the visible range. The increased spectral complexity observed for the higher capacitance, 'hard' discharges (which are nonetheless necessary for the excitation of rich analyte line spectra that includes ionic lines) unfortunately increases in every other matrix differently the likelihood of spectral overlap for complex samples.

The results reported in this chapter were possible because in Chapter V, interference-free, sensitive emission lines whose spectral responses showed a power law relationship at trace analyte concentration levels in the PVC matrix were assumed to indicate that sliding spark spectroscopy can be utilised for quantitative analysis of other samples in the concentration range of the calibration curves.

Except for unforeseen spectral line interferences, majority of the lines proved to be analytically useful, but their figures of analytical merit changed in accordance with the matrix.

Due to the complexity of matrix effects in the sliding spark, analytical response for an analyte in a difficult matrix may not be the same as for the analyte in a standard spiked in PVC.

In applied analysis, generation of working curves would require standards that match very closely the composition of the sample.

The results obtained for the certified reference Stream sediment materials above indicate that in principle, if a particular analytical model is repeated for a different matrix, or the analyte changes, it is essential to re-evaluate the performance of the calibration and the internal standard choice, including the appropriate emission lines selected, to ensure that no overlaps occur, and that the sampling (ablation) and excitation are reproducible.



Fig. 8.14 Validation of possibility for external calibration and calibration transfer in the analysis of sediment and biomaterials using sliding spark spectrometry

The bigger challenge in quantitative sliding spark spectroscopy seems to be how to discern which lines and calibration strategy to apply to a particular sample matrix since each model applies to analytes in different concentration regimes, and matrix compositions differently.

Nevertheless, the results of Fig. 8.14 indicate that it is possible to analyse, using analytical models developed in one class of sediment, other types of sediment and related matrices. This particularly works when the calibration strategy employed is matrix dilution (external calibration), coupled with internal standardisation to compensate for the matrix variations that are experienced. It is noteworthy that internal standardisation appropriately compensates for the matrix effects even in sewage sludge (indicated by ROI-02) for both Zn and Mn to the effect that the spectral response linearity validation line passes also through the matrix pointing. In Fig. 8.14 both calibration using absolute intensities, and using intensity ratios, are compared with the later yielding better matrix-compensated curves.

8.15 Analysis of Sewage Sludge

For the reasons discussed above it was decided to test the developed analytical models also on a laboratory sewage sludge standard provided by Umweltämt, Düsseldorf, Germany. The motivation of this analysis was the initial assumption that a sliding spark spectrometric method developed for the analysis of sediment as a model matrix would lend itself to application in such matrices as soil, peat, sewage sludge, fly ash, etc.

The results obtained (Table 8.20) are in a surprisingly good agreement for most elements, with that obtained using XRF and ICP, thereby validating the basic assumption. Sliding spark spectrometry is thus a potentially powerful method for the analysis of biomaterials.

A summary of the analytical figures of merit computed on the basis of the calibration based on matrix dilution is shown in Table 8.21. It can be concluded, this method of calibration is more global, and it achieves very low detection limits.

8.16 Speciation Analysis

The current and most popular trend for chemical speciation is to utilise hyphenated techniques thus yielding two-dimensional information. However, sliding spark spectroscopy demonstrates the potentials for direct speciation analysis in solid environmental matrices. In order to exploit the measured spectral lines for speciation analysis, diagnostic tests to find out if the Cu and Ti lines are also excited in sediment (as opposed to pure PVC) were made on typical samples bound in PVC. None of the speciation candidate lines were detected.

Thus, the concentration estimates in the model sediment utilised in this work represent total Cu and Ti. A software diagnostic needs to be implemented which utilises the calibration data to inspect the respective lines (at pre-determined SNR) for speciation analysis.

Based on some of the results obtained, the following may be concluded concerning the speciation possibility, which requires more research.

Vanadium

<u>Lines specific to V^{3+}</u>	<u>Lines specific to V^{4+}</u>
V II 373.602	V I 355.680
V II 310.094	V I 354.519
V I 306.695	V II 319.985
V I 292.674	V I 319.757
	V II 289.560

All the rest of the V lines measured appear in V^{5+} . That means it is possible to discriminate, qualitatively, between V^{4+} and V^{3+} , using sliding spark spectroscopy, but not between the two species with V^{5+} , since all the above lines are detected when V^{5+} is used as the test species.

Thus, the determination of V in an environmental matrix using sliding spark spectroscopy is unlikely to yield a good measure of total vanadium, instead it is more of a measure of V^{5+} .

Manganese

Lines specific to Mn²⁺

Mn I 476.238 Mn I 475.404 Mn I 401.810 Mn II 349.754

Table 8.20	Comparative method validation for sliding spark spectroscopy by transfer of the developed analytical calibration models for the
	analysis of some heavy elements in laboratory standard material (sewage sludge) in comparison with XRF and ICP techniques

Element/line	SAM calibration	SAM with	Internal Standard	External	External	Internal Standard	Certified
		Internal S	line used	calibration	calibration with	line used	concentration
					internal Standard		(ppm) or (%)
Ti II 323.452	1990±159						XRF:2130
Ti II 498.173	2010±160						ICP:
Zn I 472.216	940±80	1173±99					XRF:1330
							ICP:1182
Pb I 368.347					68.2 ± 6.8	La II 295.050	XRF:74
							ICP:89.62
Ni I 310.771					86.95±5.60	Y II 488.369	XRF:
							ICP:56.02
Co II 236.379					27.9±2.5	Y II 354.901	XRF:
							ICP:14.46
V II 297.226					54.23±4.90	Y II 488.369	XRF:
					59.18±5.80	Y II 378.870	ICP:26.89
Cr I 357.869					63.96±7.90	La II 408.672	XRF:
							ICP:46.18
Cd II 226.502					2.79±0.52	Y II 488.369	XRF:
					2.53±0.45	Y II 377.433	ICP:1.2
Fe II 274.111					6.24±0.41 %	Y II 488.369	XRF: 6 %
					7.10±0.65 %	Y II 378.870	ICP:
					6.50±0.48 %	Y II 366.461	
Mn II 257.610	490±51						XRF:
							ICP:360
Cu II 221.810					173.19±19	La II 295.050	XRF:235
							ICP:249.2
Al I 396.152				(2.45±0.23) %	(3.02±0.19) %	La II 408.672	XRF:2.65 %
				. ,			ICP:

Table 8.21Examples of calibration models and some analytical figures of merit for quantitative analysis of sediment using calibration based on
dilution with PVC with/and internal standard technique

Elem.	Spectral	Calibration based on	Linear	LOD	Dilution calibration coupled	Best internal standard	Linear correlation	LOD
	Line (nm)	dilution using relative	correlation	(ppm)	with the use of internal	element spectral line	coefficient	(ppm)
		intensity	coefficient		standard	_		
Al I	396.152	y = 0.2972x + 271.71	0.9907	254	y = 0.004x + 1.8792	La II 408 :672	0.9985	15.600
Pb I	368.347				y = 0.2004x + 0.0903	La II 295.050	0.9916	0.015
Ni I	352.454				y = 0.0579x - 0.0042	Y II 378.870	0.9932	0.002
Ni I	310.771				y = 0.0661x - 0.1719	Y II 488.369	0.9931	0.086
Co II	230.786				y = 0.0485x + 0.0758	Y II 354.901	0.9972	0.052
Co II	236.379				y = 0.7218x - 1.128	Y II 354.901	0.9972	0.052
V II	297.226				y = 0.0411x + 0.0638	Y II 488.369	0.9905	0.051
Cu II	221.810				y = 0.0164x + 0.0448	La II 295.050	0.9939	0.091
Cu II	219.226				y = 0.0588x + 0.5136	La II 362.883	0.9974	0.291
Cr II	357.869				y = 0.0586x + 0.506	La II 408 :672	0.9916	0.287
Cd II	226.502				y = 0.2685x - 0.0094	Y II 377.433	0.9913	0.001
					-			
Cd II	214.441				y = 0.9739x - 0.0728	Y II 488.369	0.9958	0.004
Fe I	274.111	y = 0.212x + 9.2553	0.9994	1.455	y = 0.0006x - 0.0728	Y II 488.369	0.9923	4.000

None of the lines listed above were selected for quantitative analysis. Thus, all the analytical lines are independent of the Mn species in the sample matrix, and the quantity of Mn detected is a good measure of total Mn.

Lead

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Line(s) specific to Pb<sup>2+</sup>
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Pb I 308. 909

The above line does not render itself suitable for quantitative analysis and was thus not selected for that purpose. This implies that the selected line(s) for the quantitative analysis of Pb provides a good measure of total Pb in the analysed matrix and quantitative speciation analysis is not possible.

<u>Titanium</u>

Among all the elements measured, Ti spectra is the richest in the number of detected lines. Among the lines detected and measured 49 can be identified which are specific to Ti ⁴⁺ (these include 5 of the lines selected for quantitative analysis, viz. Ti I 498.173, Ti II 350.489, Ti II 334.188, Ti II 328.766, Ti II 323.452).

This implies, then that only Ti II 338.783 and Ti II 338.376, if used to estimate the concentration of Ti in typical environmental matrix, would represent the total Ti content (i.e., independent of Ti^{4+} and Ti^{2+} , the two dominant states of existence of Ti as oxide in a typical environmental matrix).

Where the concentration of Ti obtained is a true measure of the total titanium, it means Ti does not exist as Ti^{2+} in the sample matrix.

Copper

Lines specific to Cu²⁺

Cu II 224.700 Cu I 222.778 Cu II 219.226 Out of the four lines selected for the quantitative analysis of Cu, only Cu II 221.810 is common to both Cu I and Cu II (in their oxide forms). This means that when the lines listed above are utilised in quantitative analysis, they lead to an estimate of Cu^{2+} rather than of total Cu concentration in the analysed sample matrix. Where the concentration of Cu obtained is a true measure of total Cu, it implies that all the Cu in the sample matrix exists as Cu^{2+} .

<u>Cobalt</u>

<u>Lines specific to Co^{3^+} </u>

Co I 352.157 Co I 347.402 Co I 339.538 Co I 258.084 Co II 255.941 Co II 234.739 Co II 231.498 Co II 231.160

None of the lines listed above was selected for quantitative analysis. It would appear the concentration estimates obtained for Co in a typical sample matrix using sliding spark spectroscopy are a true measure of total Co, and speciation analysis is not possible.

However, qualitatively this is possible. The bolded spectral lines appear both under 'soft' and 'hard' discharge conditions, when other spark source parameters are maintained.

This means qualitative speciation analysis of Co in a matrix is possible using discharge condition modulation. However, since Co^{2+} was investigated using CoS while Co^{3+} was investigated using Co₂O₃, the influence of the (anion) form would need to be considered.

IX

9.0 Conclusion and Prospects

A transient plasma propagating along the surface of a dielectric solid matrix enforced between a pair of electrodes in air at atmospheric pressure (sliding spark) enables fast electron impactbased ablative excitation of a broad range of emission spectrum suitable for simultaneous quantitative spectroscopy of the elements in the surface layers of the underlying base matrix.

Because the streamer and spark stages have been observed to be absent in vacuum surface discharges, it can be postulated that breakdown in sliding spark discharges occurs as a result of cascade ionisation of the air layer that is adsorbed onto the surface of the base matrix.

For optically thin sliding spark plasma, the small concentration of the atoms and ions present in the discharge ensures that electron collisions dominate the radiation process, and local thermal equilibrium (LTE) is established between the resonant levels, some of whose lines are strong enough to be used for trace quantitative spectroscopy of the underlying base matrix.

The search for new methods in direct solid analysis is a consequence of the drawbacks of the current quantitative methods commonly used for routine analysis of difficult solid materials. In the development of modern spectrometric methods for the direct analysis of non-conducting solids, the attention was (logically) focused on the most successful excitation source in emission spectroscopy, the ICP, where, besides direct sample introduction (DSI), much attention was paid to the electrothermal vaporisation systems (ETV). Nonetheless, ETV only achieves a maximum temperature of 2900 $^{\circ}$ C (this is even less than the 4000 $^{\circ}$ C of the DC-arc). The sliding spark, whose excitation temperature has been computed to reach as high as 17000 K, sufficient for UV excitation, has been shown to be a better analytical alternative.

Since the pioneering investigation of the characteristics of defatrons was carried out by Fünfer more than 50 years ago, hardly had any studies been dedicated to spectrochemical analysis based on the sliding spark until Golloch and co-workers recently developed the technique and applied it to the semi-quantitative sorting of plastics based on their spectroscopic signatures.

The work introduced the potential for trace quantitative analysis when strong Sn and Zn spectral line signals were detected in air at atmospheric pressure uniquely in the PVC plastics.

The primarily event in quantitative spectrochemical analysis by sliding spark spectrometry is the enhanced production of an atomic vapour from the underlying base matrix and its optimal ionisation and excitation in a spectral region where its emission spectrum can be spectrally resolved and measured.

This dissertation embodies the results of the first systematic study on the utility of the sliding spark technique in direct simultaneous trace quantitative analysis of non-conductive solids. The work has successfully advanced the sliding spark beyond semi-quantitative identification of plastics. The sliding spark technique is a simple but robust method for the analysis of heavy elements in complex, refractory solid matrices and dielectric surface layered materials.

In this conclusion, a refined study of the salient features, development of the analytical method, its application, and the main results, which highlight the versatility of the sliding spark discharge technique are summarised, followed by an outline of future perspectives.

The study reported in this dissertation has shown that:

Salient Features

Proper modulation of the sliding spark produces a high density, high temperature plasma source of many analytically useful lines excited from the atom species of the base matrix.

The spectral characteristics of the sliding spark plasma are governed by the gasdynamic processes, which depend on the thermo-physical properties of the base dielectric material. These processes are controlled by the temperature and electron density of the plasma.

By use of optical fibre transmission technique in conjunction with a holographic blazed grating spectrometer and CCD detectors, the optical emission from the sliding spark is possible to resolve spectrally and temporally and to investigate and characterise the components of the spectrum in the range $212 \le \lambda \le 511$ nm with a ≈ 0.05 nm resolution.

Because the dielectric matrix is the main source of ions in the discharge plasma, complete vaporisation of the embedded heavy elements is a pre-requisite for their quantitative analysis.

A systematic experimentation leads to the sufficient and necessary conditions (ablative, optoelectric, temporal, geometric, matrix) for the realisation of optically thin (sliding spark) plasma suitable for the trace analysis of the heavy elements in the base dielectric matrix.

Using PVC as a matrix modifier results in intense spectral lines through the formation of volatile halides. The matrix halogenation is verifiable by use of teflon. Although teflon is an equally good matrix modifier, sample preparation has to be made at a temperature of 77 K.

Theory

There is still limited theory and fundamental data available on air, atmospheric plasmas that can be accurately applied to practical problems, which arise in dielectric solid spectrochemical analysis. Fluid dynamics, for instance, of the expanding plasma plume and the shockwave front are so far unstudied.

Elucidation of the complex interrelationship between the spectral emission from the sliding spark plasma and its constituents depends on the assumption of local thermal equilibrium.

Local thermal equilibrium (LTE) is established after several μ s for emission lines in the near UV and VIS spectral range once temperatures of about 10000 K, and electron densities greater than 5 x 10²² m⁻³ are achieved. (Under LTE the spectral line intensity depends less on other factors than it does on the composition of the dielectric base matrix).

A proper formulation of the mathematical theories, which are applicable to the ionisation and excitation processes of the atoms in a dense plasma at thermal equilibrium, enables the more robust utility of sliding sparks, and offers possibilities for simulation and modelling studies.

The mathematical relations deduced for analyte quantification are experimentally verifiable.

Sample Matrix

Matrix homogeneity is crucial because the mass of sample that is atomised represents only a minute part of the sample, so that reliable analytical data is only possible when the sampled volume represents the overall composition.

The use of vibration mill for homogenisation easily achieves, for powdered solids, reproducible effects attributable to crystal structure.

Sediment is an ideal model matrix to study the utility of the sliding spark. This is because sediment constitutes concentrated dielectric matrix reservoirs of trace metals in which amounts are more magnified than those present in other adjacent phases of the environment.

Although the chemical compounds of sediment may be carbonates, hydroxides, silicates, sulphides, phosphates, or organics in various stages of crystallisation, stiochoimetry, the use of metal oxides (or carbonates) accurately simulates elemental forms in the sediment matrix.

Analytical Models

Calibration, as initially anticipated, does not prove to be the Achilles Heel in sliding spark spectrometry due to differences in ablation characteristics of different materials and the lack of suitable reference materials (homogenous, well-characterised at trace concentration level).

The developed analytical models demonstrate that the composition of sliding spark plasmas is representative of the underlying dielectric material, particularly when homologous spectral lines are used to compensate for variability in matrix ablation and analyte volatility.

Provided that a reproducible working curve is obtained for a given material, the matrix effects can largely be ignored.

Linearity and the precision of the calibration are improved by use of internal standard lines.

It is essential to choose an internal standard with similar ablation behaviour to the analyte.

Y and La are ideal elements to use as (added) internal standards, while Si and C are good (matrix-derived) internal standards to employ in sliding spark spectrometry.

The use of internal standards produces much more robust calibrations and corrects for differing ablation yield and matrix effects between complex matrices.

Additionally, internal standards correct for signal drifts in the cases where the ablation results in the heavy loading of the plasma.

Four calibration strategies are applicable in quantitative sliding spark spectroscopy:

- Standard addition method alone, using the analysis sample matrix
- Standard addition method, in conjunction with internal standardisation
- External calibration by matrix dilution with PVC or other appropriate matrix modifier
- External calibration by matrix dilution with PVC, in conjunction with internal standards.

Analytical models are successfully generated for the following elements: Mn, Ti, V, Ni, Co, Cu, Cd, Pb, Cr, Al, Fe, Zn and Hg. No model is possible for As.

The calibration of As and Hg are difficult, probably due to unrepresentative sampling.

Transfer of calibration models between related matrices (in main composition) is not reliable.

Results

The quantitative utility of the measured spectral lines depends on the element and matrix.

The sliding spark technique has potential for speciation analysis; this has been (qualitatively) demonstrated for the following elements: Mn, V, Pb, Ti, Cu and Co.

Qualitative and semi-quantitative results were obtained for the following matrices:

- Boro-silicate geological simulate
- Borax
- Polyvinyl-alcohol
- Cellulose
- Teflon
- Al-Zr ceramic powder simulate

Accurate quantitative results were obtained for the following matrices:

- PVC polymer powder
- River Rhine sediment
- Certified reference (sediment) materials
- Sewage sludge

The following elements can accurately be quantitatively analysed at trace level using sliding spark spectrometry: Mn, Ti, V, Ni, Co, Cu, Cr, Al, Fe and Zn.

The accurate analysis of Cd and Pb, particularly Pb, is plagued with difficulties, probably due to their high volatility or unrepresentative sampling owing to elemental fractionation.

The sliding spark detection limits for quantitative analysis vary from several hundred ppb to few tens of ppm depending on the element, spectral line and calibration strategy employed.

The sliding spark technique has a satisfactory reproducibility at ≤ 12 %; the precision of the method can be characterised by a confidence interval of $\pm (0.5 - 10)$ % (better precision is likely to be obtained when peak area is used in the signal processing); and the accuracy by relative efficiency of $\approx 0 - 10$ %.

These analytical figures of merit are all in the order of the same standard error as observed from comparisons of traditional direct solid analysis methods such as XRF, one of the methods against which the analytical results have been compared.

Application

Sliding spark spectrometry works successfully in the detection of heavy trace elements in powdered, non-conducting materials. It may therefore be applied to samples such as:

- Spent nuclear fuel components
- Break linings wear powder
- Vehicular exhaust particulates
- Coal fly ash
- Cement
- Rocks and ore samples
- Waste glasses
- Plastic polymers
- Non-conductive solid substrates
- Solid biomaterials

Geology is probably the single most active area of application of sliding spark spectroscopy. (Geological samples frequently contain refractory minerals that are not readily decomposed).

Small particle size environmental aerosols could also be analysed. They would need to be collected/ sorbed on PVC impregnated cellulose collectors. Nuclepore filters would need to be re-made to suit the analysis geometry. The sample cell would require a novel development.

Advantages

Sliding spark spectrometry

- Provides spatially resolved quantitative and qualitative elemental/molecular information.
- Is an immediate, simultaneous, *in situ* analysis technique.
- Is a direct solid analysis method applicable to complex non-conducting materials.
- Can readily be adapted for remote computerised analysis using optical fibre.
- Is both time- and cost-effective, and provides good precision and relative accuracy.
- Has potential for speciation analysis, which has become a great challenge in the last decade due to its impact in the environmental sciences, medicine, agroalimentry, etc.

New spark sources can easily be constructed, as the power source is simple when compared to the RF power sources used to generate and maintain ICP plasmas or to laser systems.

There is a higher flexibility in analytical line selection with possibilities of multivariate calibration because the technique relies on the line-rich UV/VIS spectrum range.

Sample preparation procedure is almost absent or easy and does not need any liquid steps.

Disadvantages

Sliding spark spectrometry

- Is subject to extreme matrix effects especially at minor and major analyte concentration.
- Suffers from random shot-to-shot variation in the sample matrix ablation.
- Is characterised by a high continuum radiation due to bremsstrahlung in the spectral emission region; the emission is continuous and overlaps most of the analyte lines.
- Is essentially a bulk technique, and exclusively surface analytical possibilities are not easily envisioned in the near future.
- Is undermined by the significant spectral broadening due to Doppler, collisional and Starkeffects, by virtue of the high ion (plasma) density in the spectral emission region.
- Is plagued by self-absorption and line reversal because the middle hot plasma zone is surrounded by a sheath of cool, rapidly expanding discharge.
- Experiences line interferences (wing, direct, and broadening) and continuum overlaps.

Versatility

The utility of chlorination from the PVC as a matrix modifier opens up investigations in the use of materials such as AgCl, BaF₂, NH₄Cl, PTFE, as matrix volatilisation aids.

Simultaneous halogenation using CF₂Cl₂ may improve the evaporation of the trace elements.

Where a non-powdered solid is analysed, a stream of purge gas, like freon, may be pre-sprayed on the sample surface, separated a few μ s from the time of the spark initiation.

Sample excitation may be improved by engineering sliding spark sources that reduce the extent of melting but which enhance the physical ablation process. A high physical ablation rate achieves both high sensitivities and high power of detection.

If oxygen, water vapour (which reduces the sputtering yield and the ionisation of the matrix atoms in the plasma), and other species, which absorb electromagnetic radiation in UV range are eliminated, this would ensure a high optical transmission down to 125 nm, and the removal of molecular bands and spectral interference. (A little inert gas purge would enhance the spectral intensities and reduce the effects of background and cyanogen (CN) emissions.)

The use of partial vacuum may improve the linearity and sensitivity of the working curves.

The plasma emission may be enhanced by, for example, applying a capacitive discharge across the rising, expanding plasma plume. An auxiliary excitation system may also be implemented by application of a spark or arc discharge: A pair of pure carbon electrodes may be positioned a millimetre or so above the underlying matrix. A capacitive circuit can then be charged to a potential difference just below that of the sliding spark breakdown potential.

The rising plasma plume will intercept the electrode gap and initiate a capacitive discharge, releasing an energy pulse into the vapour. This may also be externally triggered such that the vapour enhancement is timed to coincide with the highest vapour densities. Alternatively, an axial discharge may be positioned a few mm above the base matrix, which is itself connected to earth. Higher discharge voltages can be used, with consequently higher energies being deposited in the vapour plume. A laser may also be used.

Where however vaporisation is the problem for a given element and/matrix, spark excitation of the vapour cannot improve detection, unless the spark were functioning as a secondary source of vaporisation.

Another novel attempt at plasma enhancement would be to surround the plasma with a magnetic field. A study however on the influence of magnetic fields of various forms on the formation and development of sliding sparks in air at atmospheric pressure is (still) wanting.

Future Perspective

The sliding spark is a rich source of excited atoms and ions originating from the dielectric base matrix, which may be exploited under suitable criteria for hyphenation (e.g., sliding spark mass spectrometry).

Sliding spark spectrometry also detects molecular, including radical species spectra and lots of 'cool' neutral atom species and thus possesses the feasibility for the elucidation of structural and molecular information if temporal gating techniques are used.

In the typical pulsed discharge plasma, atomic vapour in the post-discharge regions has a lifetime of almost 300 μ s following the execution of the excitation pulse, but ionised species reach peak intensity in a few μ s. While this means that for quantitative trace elemental spectroscopy it is imperative to find integration times for which good signal-to-noise-ratio is achieved (i.e., use a typical delay time necessary to gate passed the bright continuum radiation due to recombination so as to detect only the more persistent emission radiation of the analyte species excited in the discharge plasma), it also implies that if the spark source frequency is set to greater than 3 kHz, atomic vapour would continuously be present between the electrodes, and a fluorescence component to the emission is possible. Thus the sliding spark source at high repetition rates may be optimised to be a vapour source for combined emission, fluorescence, and absorption spectroscopy. The source may then be operated under 'soft' discharge mode in order to primarily excite few but most intense of the atom lines.

Applications for micro sliding spark can be envisaged for the study of the spatial relationships of dielectric surfaces (zonation). So are applications in near-surface emission tomography.

Better signal-background ratios may be achieved by optimising the instrument to observe emission either away from or in the discharge axis. Neutral species occur primarily in the cooler wings of the plasma and the ionic emission occurs primarily along the plasma axis.

Time–resolved sliding spark spectroscopy should give a clearer picture of the discharge development with high temporal resolution. For the production of time-resolved spectra, an electronically controlled source operating with a high precision in time is needed. Recently developed CCDs allow measurements of spectral intervals with time resolutions of ns. The differences in decay time between ionic an atomic lines can provide a good mechanistic insight into, and suggest additional practical applications of, the sliding spark discharges.

In order to exploit fully the sliding spark discharge plasma for accurate quantitative analysis, it requires a more exact knowledge of its temperature and density. Due to the transitory nature of sliding spark-produced plasmas, atomic and ionic populations are rapidly varying functions of time and position – the determined temperature of the plasma shows this variations. Thermodynamic equilibrium can only be assumed to prevail for a given point and time in the plasma development. At this point a single temperature, defines the excitation and ionisation state of the plasma and LTE can truly be said to occur. Internal standardisation thus requires choice of lines that ensures the species are in the same plasma region.

A more comprehensive optimisation of sliding spark spectrometry asks for detailed knowledge on the fundamental processes of sample volatilisation and signal generation. The spark source should be optimised in the physical ablation so that the maximum amount of sample is vaporised with minimum ejection of molten material. Although the thermal interaction of plasma with sample may be reduced with state-of-the-art source, only separation of the vaporisation and excitation can lead to lower matrix effects and detection of less complex emission spectra. Pre-programmed, variable-inductance, sources, are necessary.

The future of sliding spark spectroscopy lies with the development of a fully automated portable system, with data processing facilities, for on-line and *in situ* analysis. Automated quantitative and semi-quantitative analysis routines using spectral databases, coupled with multivariate statistical analysis and spectral libraries should lead to a broader range of the technique's applicability. An 'expert' software can for instance integrate the optimal, appropriate number of ablation shots for each element, spectral line, and sample matrix. The use of neural networks then becomes important.

When considering future improvements, however, it should be borne in mind that any developments ought to be weighed against the risk of reducing the technique's simplicity.

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