THE ANALYSIS OF SEDIMENT REFERENCE MATERIALS BY DIRECT SAMPLE INSERTION INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

by

Laurent Blain

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Department of Chemistry
McGill University
Montréal, Québec

September 1991

ABSTRACT

A procedure for the analysis of sediment samples by their direct insertion into an inductively coupled plasma is described. A novel probe design that consisted of a pellet pressed from a mixture of sample and briquetting graphite was evaluated using graphite based metal oxide dc arc standards. These pellets were carried into the plasma held in wire baskets. By increasing the mass of sample inserted in the plasma at once, without encroaching further in the zone where inductive coupling occurs in the discharge, this probe provided a commensurate improvement of detection limits. However, the sudden release of large quantities of silicon into the plasma's core upon decomposition of the silicate matrix of sediments seriously impaired its analytical performance.

When graphite cups were used to carry the pellets into the plasma, it was found that the presence of walls confined the escaping gases into an axial channel through the plasma's tailflame. The geometry of the cups was optimized to temporally resolve the signals of volatile elements from physical and spectral interferences of silicon. The determination of these elements in a sediment reference material (PACS-1) by the method of standard additions was then carried out, with a typical relative error of less than 10%. It was found that the chemical form of the analytes in the spiking standards did not need to be matched to that in the sediment, at least for these elements. The selection of a volatility enhancing thermochemical additive is discussed, and it is shown that refractory elements are also amenable to these assays.

RESUME

Nous décrivons une méthode pour l'analyse d'échantillons de sédiments par insertion directe dans le plasma inductif (ICP). Le mérite des nouvelles sondes préparées à partir d'un mélange d'échantillon et de poudre de graphite est évalué par l'analyse de mélanges standard à base d'oxydes métalliques et de graphite. Ces sondes sont des briquettes tenues par un panier de tungstène, et leur avantage principal est de permettre l'insertion de masses accrues d'échantillon dans le plasma sans envahir la région où le transfert d'énergie par induction est le plus efficace. Par conséquent, nous avons constaté une nette amélioration des limites de détection. Cependant, toutes nos tentatives d'analyser des sédiments avec ces sondes se sont soldées d'un échec. Il appert que de larges volumes de vapeurs de silicium sont émis par ces échantillons, compromettant ainsi la viabilité analytique du plasma.

Nous avons alors eu recours à des électrodes de graphite pour porter ces briquettes d'échantillon, afin que leurs parois restreignent les vapeurs atomiques dans un jet le long de l'axe central du plasma. Nous avons optimisé les dimensions du cratère afin de retarder l'apparition du silicium dans le plasma, et ainsi permettre l'observation aisée du signal des éléments à volatilité élevée et intermédiaire. Nous avons effectué le dosage de ces éléments dans un sédiment de référence, le PACS-1, par l'addition incrémentale d'un mélange standard à base d'oxydes métalliques et de graphite. Les résultats obtenus sont comparables à ceux des méthodes traditionelles, c'est à dire une erreur typique en dessous de 10%. De plus, nous avons découvert qu'il n'était pas nécessaire de s'assurer que la

composition chimique du standard ajouté soit conforme à l'échantillon, pour ces éléments du moins. Enfin, nous nous penchons sur le choix d'un agent thermochimique pour accroitre la volatilization des éléments réfractaires.

ACKNOWLEDGEMENTS

I would like to express my thanks to Professor Eric D. Salin for his advice and support through this project. His patience, and occasional loss thereof, have helped to bring this thesis from the realm of conjectures into tangible reality.

Three others have made significant contributions to this project and deserve many thanks. First in chronological order is Dave Boomer of the Ontario Ministry of the Environment, for his interest in the project and many helpful discussions. Guy Légère comes next, for all the hours spent upgrading the ATOMCOMP 97500 direct reader at Technical Service Laboratories, and the continued technical support. Finally, Dr. Vassilios Karanassios who had the patience to sit through many heated debates on vaporization mechanisms and thermochemical additives.

I would like to thank everyone in Prof. Salin's group for their editing assistance and for making my stay a pleasant one.

I would also like to thank the following :

Dr. R.L.A. Sing for getting me started on the DSID

A. Kluck and W. Bastian for help in designing the modified DSID and for building it

G. Kopp for help in designing the modified DSI torch

Financial support in the form of Post-Graduate Awards from the Natural Sciences and Engineering Research Council of Canada (NSERC) and Le Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR) as well as funding from the Ontario Ministry of the Environment are greatly appreciated.

Finally, I would like to thank the many friends who contributed in their own way. Six stand out and deserve special mention :

Clevys and Michelle, who helped me through the long days of experimental work

Tim, Shaune, Loy and Sal who stood by me during the *Barton Fink* days.

TABLE OF CONTENTS

Figures

Figures

LIST OF TABLES

LIST OF TABLES

Figure 3

Signals observed at the As, Cd, Hg, Pb and Zn channels during the preheat step prior to the insertion of 1:8 PACS-1/graphite pellets held in wire baskets

Figure 4

Time profile of the baseline interference observed a few seconds after the insertion of a pellet of 1:8 PACS-1 in graphite at the Hg, Zn, Cu, Pb and Cd channels in ascending order. The top trace is the signal of Si, included to emphasize the correlation of the baseline interference with that signal. The time profile of the signals at the first five channels was recorded with the spectrum shifter set farthest from its on-line position.

Figure 5

Two slices across the time profile of the signal at the channel of Pb after the insertion of a pellet of 1:8 PACS-1/graphite. One, labelled signal, was extracted from the early part of the time profile, during the peak of Pb. The other, labelled interference, was extracted from a later part of the exposure, during the stray light's broad hump.

Figure 6

Calculation of the two parameters I_{peak} and $N_{back.}$ from the on-line and off-line signals. I_{peak} is the difference between on-line and off-line intensities at the peak's maximum, and $N_{back.}$ is the standard deviation of the off-line signal calculated over the duration of the peak only (as indicated by the box around the off-line trace).

Figure 7

Average ratio of I_{peak} to $N_{back.}$ for Pb, plotted as a function of viewing height for each cup geometry studied.

Figure 8

Average ratio of I_{peak} to $N_{back.}$ for Cd, Hg, Pb and Zn, plotted as a function of the graphite cup's height.

Figure 9.a)-

Calculation of the measure of separation R', the ratio of the distance between the two peaks and the width at half height of the first peak.

Figure 9.b)-

Effect of the graphite cup's wall thickness on the temporal resolution of the signal of Pb (1) from a spectral interference (2).

Traces : (a) - 11/64" id, 3/16" od
(b) - 5/32" id, 3/16" od
(c) - 1/8" id, 3/16" od

Figure 9.c)-

Effect of the depth of the graphite cup's well on the temporal resolution of the signal of Pb (1) from a spectral interference (2).

Traces : (a) - 1/4" depth
(b) - 3/8" depth

Figure 10.a)-

The measure of separation R' plotted as a function of the temporal separation between the two peaks of Figures 9-b) and 9-c).

Figure 10.b)-

The measure of separation R' plotted as a function of graphite cup geometry.

Narrow - 11/64" id, 1/4" depth
Narrow & deep - 11/64" id, 3/8" depth
Medium - 5/32" id, 1/4" depth
Medium & deep - 5/32" id, 3/8" depth
Wide - 1/8" id, 1/4" depth

Figure 11

The combined effect of wall thickness, well depth and plasma RF power on the temporal resolution of analyte signal (1st peak, Pb) from a spectral overlap (2nd peak, Fe) and a stray light interference (3rd peak, Si)

Traces : (a) - medium walls, shallow well @ 1.5 kW
(b) - medium walls, deep well @ 1.5 kW
(c) - medium walls, deep well @ 2.0 kW

Figure 12.a)-

Signal of Hg after the multivariate optimization of DSI and ICP parameters

probe : 125 mg pellet of 1:5 PACS-1/graphite
category : very volatile
concentration in PACS-1 : 4.57 ppm

Figure 12.b)-

Signal of Cd after the multivariate optimization of DSI and ICP parameters

probe : 125 mg pellet of 1:5 PACS-1/graphite

category : volatile

concentration : 2.38 ppm

Figure 12.c)-

Signal of Pb after the multivariate optimization of DSI and ICP parameters, illustrating temporal resolution of interferences

probe : 125 mg pellet of 1:5 PACS-1/graphite

category : volatile

concentration : 404 ppm

Figure 12.d)-

Signal of Mn after the multivariate optimization of DSI and ICP parameters

probe : 125 mg pellet of 1:5 PACS-1/graphite

category : intermediate volatility

concentration : 470 ppm

Figure 12.e)-

Signal of Fe after the multivariate optimization of DSI and ICP parameters

probe : 125 mg pellet of 1:5 PACS-1/graphite

category : refractory

concentration : 6.96 %

Figure 13.a)-

Signal of Al from the insertion a 125 mg pellet of 1:1:5 AgCl/PACS-1/graphite.

concentration : 12.23 %

wavelength span : 0.064 nm in 32 steps

Figure 13.b)-

Signal of Co from the insertion a 125 mg pellet of 1:1:5 AgCl/PACS-1/graphite.

concentration : 17.5 ppm

wavelength span : 0.064 nm in 32 steps

CHAPTER 4

Methodological Solutions for the Analysis of Sediment Samples by Direct Sample Insertion Inductively Coupled Plasma Atomic Emission

Figure 4

Calibration curves obtained by the method of standard additions for six elements in PACS-1

i)- volatile elements

a)- Cd @ 2.38 ppm
spiking standard : SPEX g-standards
b)- Hg @ 4.57 ppm
spiking standard : SPEX g-standards
c)- Pb @ 404 ppm
spiking standard : SPEX g-standards
d)- Zn @ 824 ppm
spiking standard : SPEX g-standards

ii)- elements of intermediate volatility

e)- Cu @ 452 ppm
spiking standard : SPEX g-standards
f)- Mn @ 470 ppm
spiking standard : SPEX g-standards

CHAPTER 5 133

Application of AgCl as a Thermochemical Additive for the Determination of Refractory Elements in Sediment Samples by Direct Sample Insertion Inductively Coupled Plasma Atomic Emission Spectrometry

Figure 1

DSI probes consisting of a 125 mg pellet of sample held in an undercut graphite cup, used for the determination of refractory elements in sediment samples using thermochemical additives (o.d. : 3/16", i.d. : 11/64", sup depth : 3/8")

Figure 2

Signal recorded at the 267.716 nm channel of Cr after the insertion of a pellet pressed from a 1:1:5 mixture of AgCl, PACS-1 and graphite.

wavelength span : 0.075 nm
duration : 20 s

Figure 3

Signal recorded at the 267.716 nm channel of Cr using a simple exposure with a single off-line background position.

on-line : 267.716 nm

off-line : 267.707 nm

Figure 4

Signal recorded at the 267.716 nm channel of Cr using an exposure consisting of 50 repeat scans across 32 spectrum shifter positions separated by 0.002 nm.

duration : 10 s

Figure 5

Offset replicate signals for Cr, after the insertion of 5 pellets pressed from a 1:1:5 mixture of AgCl, PACS-1 and graphite.

RSD on peak area : 13%

Figure 6

Offset replicate signals for Zn, after the insertion of 5 pellets pressed from a 1:5 mixture of PACS-1 and graphite.

RSD on peak area : 7%

Figure 7.a)-

Calibration curve obtained by the method of standard additions for Co

slope = $(2.5+/-0.2)x10^4$

Figure 7.b)-

Calibration curve obtained by the method of standard additions for Cr

slope = $(1.1+/-0.1)x10^4$

Figure 7.c)-

Calibration curve obtained by the method of standard additions for Ni

slope = $(5.2+/-0.1)x10^4$

Figure 7.d)-

Calibration curve obtained by the method of standard additions for Co

slope = $(4.4+/-0.4)x10^4$

CHAPTER 1

Introduction

INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry (AES) is now a well established technique for elemental analyses at the major, minor and trace levels in a wide range of applications [1,2,3,4]. A comparison of the performance characteristics of inductively coupled plasmas with those of a conceptual ideal atomic emission source is revealing of the reasons behind the success of this technique, and it also points the way in which the technique is heading.

Among the features most often attributed to the ideal atomic emission source are that it completely atomizes all elements, has sufficient energy to excite all the elements, has little or no background emission, and that it provides an inert chemical environment. On all these points the inductively coupled plasma fares well, chiefly because of its high temperature and long residence times. Using argon as the support gas ensures that the free atoms are formed in an environment that is chemically inert. Finally, its high electron number density makes this source virtually free from ionization interferences.

On other scores, however, the plasma falls short of the mark. For example, an ideal emission source should be tolerant to various solution conditions and solvents, it should accept not only solutions, but gases and solids as well, it should be inexpensive to purchase and maintain, and it should be easy to operate. Although the inductively coupled plasma is a reproducible source and capable of producing accurate and precise results, it requires considerable skill to do so. Indeed, a textbook on spectrochemical analysis warns the reader that "... considerable training is required to become an efficient and knowledgeable user of ICP systems" [1]. Complete inductively coupled plasma systems start in the $50,000 range and can be significantly more expensive, particularly when a mass spectrometer is used as the detector instead of an optical system. Although new low flow torch designs reduce the typical gas consumptions of ICP, operation and maintenance costs are substantial.

The ICP's requirements on sample format remain one of its major drawbacks, and ironically these limitations are not imposed by the nature of the source itself but by the sample introduction devices that are used. The most common sample introduction device is a pneumatic nebulizer which uses a jet of compressed gas to aspirate and nebulize the solution. Because the range of droplet sizes produced by these device can be wide, typically from 1 to 50 μm, the mist then enters a spray chamber, where most of the droplets with a diameter above a certain cutoff are removed from the stream and drained away. Only the smaller droplets, less than 3% of the original sample, are finally transported to the atomization source. Special nebulizers are available that will handle solutions with a higher content of dissolved solids than the pneumatic nebulizers can take, such as the Babington nebulizers, or that generate finer mists, such as ultrasonic nebulizers. This comment notwithstanding, it is a general rule of nebulizer based systems that they are very intolerant of changes in the physical properties of the sample solutions. At any rate, such systems can clearly physical properties, such as viscosity and surface tension, can have a profound impact on transport mechanisms. Direct sample insertion should thus not only result in increased sensitivity but also in improved precision and more robust calibration curves.

In this technique, samples are placed into or onto a carrying probe that is most commonly a graphite cup electrode such as those commonly used in dc arc emission, and this probe is inserted into the central core of the plasma. A torch similar to the conventional ones is used, except that the injector tube is either completely removed or it is replaced by a silica tube through which the probe can be moved. The probe is supported by an insulating rod at the end of a shaft which is either attached to a mechanical system or pneumatically driven.

A number of workers [8] have made steady progress in the development of methods for the direct insertion of samples in the inductively coupled plasma, mostly for liquids. This work has been carried out on three fronts, often concurrently, the design of the direct sample insertion device (DSID) itself, modifications to the hardware and software of existing atomic emission spectrometers to accommodate the transient signals of DSI, and the characterization of DSI with various types of sample. This section will survey the development of DSI from its early days to its current status, roughly in chronological order. In some instances it would have been awkward to break up the work of some groups, even if it spread over a few years, and some allowances have been made where necessary, for the sake of continuity.

Kirkbright and Walton [9] reported a direct sample insertion device (DSID) that was manually operated, and consisted of a standard graphite support mounted on an insulating handle, that could be pushed up to the plasma through a widened injector tube. Small volumes of sample solution were deposited on the graphite support and desolvated by external heating, since attempts at desolvation in proximity of the plasma using the thermal and inductive heating had been unsuccessful. Upon insertion of the probe in the plasma, the latter's background emission intensity fell, a consistent feature in direct sample insertion. A few milliseconds after the insertion of the probe, peak shaped transient signals appeared that lasted less than ten seconds. It was found that the height of the peaks increased with shallower cups, and the geometry of the probes was finally reduced to that of flat rods. Absolute detection limits ranged from 6 to 60 pg for volatile elements, and precision was acceptable at 5 to 10% RSD. In a later report, Kirkbright and Li-Xing [10] reported the determination of refractory elements with a slightly modified version of that DSID, where an injector gas flow was provided. A 0.1% mixture of trifluoromethane (Freon 23) in argon was employed as the injector gas to cause the preferential formation of volatile halides of Ti, U, and Zr, rather than their refractory carbides. They reported that improvements in the detection limits of more than two orders of magnitude were obtained for these elements with this mixture.

Meanwhile, Haraguchi and Abdullah published two reports on a mechanical DSID for a continuously operating ICP for the analysis of microliter volumes of solution samples [11,12]. With their platform elevated graphite cup direct insertion device, these authors were able to perform a sequence of drying, ashing and vaporization steps sequentially. The earlier

DSID designs required that the sample be dried externally, with an i.r. lamp or a heat gun for example. Mention is made by these authors of the difficulties involved in recording the transient signals of DSI, and the authors reported it was "... difficult to time the emission signal integration in the manual and mechanical insertion procedure because of the fractional vaporization of different elements". They proposed that automation of the cup insertion device using a microprocessor controlled stepping motor was desirable to improve the analytical figures of merit.

With their mechanical prototype, Haraguchi and Abdullah undertook the univariate optimization of DSI and plasma parameters, such as rod height, ashing time, applied power and observation height [12]. They used the signal to background ratios (SBR) of the integrated DSI signals as the optimization criterion, and found that compromise conditions had to be established for multielement determinations. Once compromise conditions had been established for 15 elements, sub-nanogram limits of detection were achieved with 10 υL volumes of solution, with relative standard deviations of 2 to 12% and linear calibration curves over 4 to 6 orders of magnitude. The effect of commonly used acids on drying conditions, ashing conditions, and analytical signal, was investigated. It is reported that HCl and HNO_3 had little effect on the emission signals whereas $HClO_4$ and H_2SO_4 suppressed the signals of some elements. Two NIST reference materials, Spinach (SRM 1570) and Orchard Leaves (SRM 1571) were then digested with mixtures of HNO_3 and $HClO_4$ and analyzed by DSI. The results were generally in good agreement with the NIST certified values, but for some of the trace elements interferences from the major elements were significant.

Around the same time, early in the history of DSI, two interesting applications for the direct analysis of solids were reported. Prack and Bastians [13] investigated the use of a DSID for the speciation of vanadium and lead salts, while Page and his group [19,20] were adapting the carrier distillation technique of dc arc to DSI-ICP-AES. Prack and Bastians [13] implemented an evolved gas analysis (EGA) method that used an ICP both as the source of heat and as the detector. Evolved gas analysis is a thermal analytical method in which gases released from a sample are monitored as a function of temperature [14,15,16,17,18]. This technique holds great promise in the area of solid sample speciation.

Previous effort had shown that while EGA with MS or AES may have had the potential for metal speciation, little progress had been made in these areas. The existing EGA techniques for inorganic compounds suffered from inadequate upper operating temperatures and/or insufficient temperature control. As a result, the evolution of compounds with similar boiling points could not be resolved, and high boiling solids could not be vaporized.

In the system proposed by Prack and Bastians [13], heating of the sample was achieved by slowly moving the sample along the vertical central axis of the torch. As the samples were heated, its components vaporized at characteristic temperatures into the supporting argon of the plasma. Detection was based upon the observation of atomic emission of the elements of interest from the evolved gases. For speciation to be achieved by this method, it was necessary to determine the differences in vaporization temperatures of different compounds of the same element.

Here, identification of a given compound was based on the position of the cup at the time of evolution of the element.

For its part, Page's group determined to combine the high sensitivity of the method of carrier distillation into the dc arc with the reproducibility of ICP techniques. They designed a simple spring loaded direct insertion device that allowed a Scribner-Mullin dc arc electrode to be pushed to a set position into the plasma. A graphite lid with a central opening was used to force the analyte vapors into the central zone of the plasma. In a first publication [19], they reported the selective volatilization of Cd, Cu, K, Na, Ni and Pb from uranium oxide powder using 5% AgCl as the carrier, and the next year [20] they extended this procedure to the determination of B, Be, Co, Cr, Fe, and Mn, in the same matrix. These authors speculated that the mode of release of analyte vapors from the solid samples in the ICP is similar to that in the dc arc, by thermal vaporization. They also reported that experiments to estimate the physical temperature of the electrode in a 1.4 kW argon ICP were carried out using metals with different melting points, which indicated that it was somewhat lower than that observed with the dc arc, about 1800^{o}C.

The insertion of a probe in the plasma profoundly affects its impedance and its gas flows. These effects have not been clearly unraveled but seem related to the geometry and the mass of the probe [21]. Thus, the impact of the probe's geometry on the size of the signal, its time profile, and its reproducibility has been examined [21,22,23,24]. Barnett et al. [22] studied four different geometries of the graphite cups with respect to their heating characteristics, and found that the supports with the lowest mass and the narrowest stem heated faster, and usually yielded narrower and taller peaks. On the other hand, they also found that the support geometry had no influence on reproducibility. Shao and Horlick [23] studied the effect of electrode diameter on the signal's time profile, and found that the narrower probes resulted in taller peaks that decayed rapidly. However, in contrast to Barnett et al. [22], they found that the cup diameter also affected precision, and that an intermediate cup size resulted in better precision.

Zaray et al. [21] used two different types of graphite cups both with and without covers and found that the difference between net line intensities with and without covers was small, but that the background intensities differed markedly. They also found that the smaller cups heated faster and reached higher temperatures. Umemoto and Kubota [24] also investigated the effect of probe geometry on signal. They used five different probe geometries, and found that the peak heights of many elements decreased with increasing cup thickness. They also determined that the influence of the plasma's applied power was correlated with the thickness of the cups, and that appropriate selection of the cup thickness in compliance with rf power is necessary.

In the same vein, Karanassios, Horlick and Abdullah have recently published a report [25] on the characterization of a DSID for ICP-AES where the analyte emission temporal behavior was surveyed for several elements with a range of vaporization properties. The emission time behavior for most elements was characterized as a function of the probe's geometry and composition, the insertion speed and position as well as the applied plasma power. A long undercut graphite electrode was found to be the best shape out of all the probe geometries tested. It was also found that the probe should be inserted rapidly to a position corresponding to the top of the ICP's load coil, and that the plasma power should be high (1.75-2.00 kW) in order to attain best analytical performance.

Salin and Habib [26] gave the idea of the graphite electrode, another common appellation for the graphite cup probes, new meaning when they investigated the use of electrochemical preconcentration by cathodic deposition onto the body of a graphite rod which was then dried and inserted into the plasma. Their DSID was manually operated and still required that the plasma be extinguished between insertions. For these workers, uninterrupted operation of the plasma was not preferable anyway since they were relying on inductive heating to dry the electrodes prior to their insertion. The main thrust of this paper was to demonstrate that the electrodeposition step improves detection limits. For example, the detection limit of copper was lowered from 1.2 ng/mL with a 5 min deposition period to 0.07 ng/mL after a 2 h deposition.

A year later, Habib and Salin [27] published another paper which discussed the use of cathodic deposition to extract selected elements from difficult matrices such as sea water. The practical utility of the electrodeposition technique was tested with the determination of copper in a synthetic seawater sample, and it was found that small amounts of NaCl remained on the graphite electrode. These were sufficient to cause stray light spectral interferences in the ICP determination, and that an electrode washing step with 0.1 M perchloric acid was necessary. Unfortunately, the sensitivity gains accrued from electrodeposition did not unequivocally compensate for the added complexity of the instrument and sample preparation procedure. Indeed, an improvement factor of only 17 ensued from increasing the plating time from 5 min to 120 min for copper, and even less for nickel at 13.

The same idea was taken up a few years later by Haraguchi and Abdullah [28], who used controlled potential cathodic deposition to preconcentrate and separate trace elements from artificial sea water. They found that after a comprehensive optimization of the electrolysis parameters by a univariate search method it was possible to preconcentrate trace metals by a factor of 30 to 300, and to separate them from major matrix components such as NaCl, KCl and $MgCl_2$ in the electrolyte solution. The detection limits of eight elements were lowered down to the pg/mL level, with relative standard deviations of 2 to 11%. The authors suggested that this technique could find wide applicability for the determination of trace metals in seawater and biological fluids which are usually difficult to analyze by ICP-AES with the use of conventional sample introduction devices.

Concurrently, Salin and Sing [29,30] were investigating the possibility of analyzing small volumes of solution by holding them onto a wire loop, which was dried under the plasma prior to its insertion. The use of a wire loop was found to result in rapid volatilization of the sample and, in turn, high momentary concentrations of the analyte in the viewing zone. Tungsten wire was used for the majority of the studies, but tantalum was also used to alleviate intractable spectral interferences arising from the spectral and temporal overlap of tungsten's signal with those of some analytes. Detection limits in the picogram to subpicogram range were reported, and it was found that they could be improved by a factor of at least 10 using multidrop insertions [30].

Salin and Monasterios [31] reported the direct determination of trace elements in human hair with a graphite cup DSID. The goal of their project was to demonstrate the potential of DSI for clinical and forensic analyses, and it was felt that human head hair provided an easily obtainable, yet still representative, sample of this type. It was found that ground hair foamed and sputtered out of the graphite cup after insertion into the plasma, so a deeper well electrode was designed and used with and without a boiler cap, with no significant improvement of the burn. On the other hand, when 5 to 15 mm strands of hair were used instead, the burn proceeded smoothly and the reproducibility of the measurements was typical of this type of sample. The authors also found that quantitation by the method of standard additions with aqueous standards did not yield accurate results.

The automation of the DSID has been the subject of many publications on direct sample insertion, because otherwise much of the technique's potential is wasted [12,25]. Kirkbright and Li-Xing replaced their original DSID with a microprocessor controlled stepper motor driven screw assembly [32]. With this device, it was now possible to precisely control the movement and position of the probe, and drying by thermal and inductive heating could be carried out directly under the ignited plasma. Abdullah and Haraguchi [33] automated their DSID by providing a stepper motor driven belt to raise and lower the platform of their previous device [11]. Sing and Salin [30] have also published a report on a simple stepper motor driven system, similar in design to that of Abdullah and Haraguchi.

Horlick's group has published three automated DSID designs [34,23,36]. Pettit and Horlick [34] described a DSID in which sample carrying cups could be sequentially and automatically inserted in the ICP discharge using a pneumatically activated transport system. This system allowed height programming so that drying and ashing steps could be performed in situ. Karanassios and Horlick [35] recently reported a similar computer controlled system with both pneumatic and mechanical control of the insertion. Shao and Horlick [23] proposed a system based on a reversible motor that drove a leadscrew, which in turn moved a cup holder up and down the plasma torch. Karanassios and Horlick [36] recently published a report on a DSID for SCIEX ELAN ICP-MS instrument, which is operated horizontally. Whereas in ICP-AES the central channel of the plasma is imaged laterally on the spectrometer's entrance slit, the central channel is sampled head on in ICP-MS. Various design considerations were simplified by operating the plasma horizontally, which dictates that the DSID be modified accordingly for ICP-MS. Karanassios and Horlick felt that the subsequent use of a robot arm to load the probes onto the DSID required that the latter start from a vertical position. The result is a system that makes clever use of available mechanical devices to achieve a smooth transition from a vertical position to the final horizontal alignment. On the other hand, Sing and Salin [37] have simply laid their vertical stepper motor driven DSID on its back and installed it on the same instrument, with minor adjustments.

Zaray et al. [21] reported a DSID design in which a dc motor drives a screw in a reversible direction and at different velocities, and this unit moves the sample carrier along two guide stubs. The start and final positions of the sample carrier are controlled by prepositioned microswitches. A common feature of all these automated systems is that they offer programmable insertion sequences that can include many steps prior to the insertion of the probe in the plasma, and that the final insertion sequence can now be precisely controlled. Where they differ is in the particular mechanism by which the sample carrier is moved, which in turn imposes distinct control strategies. As a rule, in pneumatic systems the various positions of the sample carrier are controlled by a set of switches [35], and likewise in systems that are based on free-running motors [21,23]. On the other hand, the precision of which a stepper motor is capable allows devices that use them to be completely put under software control [23,32,33,30].

Haraguchi and Abdullah [33] used their automated DSID for the direct analysis of a series of standard reference plant materials. Between 1 and 5 mg of powdered plant samples were ashed under the base of the plasma, and it was found that the use of a graphite lid on the top of the cup prevented the loss of sample by spitting. Furthermore, when the probe was introduced in the plasma, the central hole of the lid helped confine the atomic vapor in the axial channel of the plasma. The absolute detection limits for 18 elements in a cellulose matrix were at the nanogram level with better than 13% precision, and the analytical results of NBS Orchard Leaves showed good agreement with the certified values.

That same year, Lorber and Goldbart [38] reported on their design of a horizontally operated DSID for ICP-AES, in which the probe is inserted laterally into the plasma instead of axially. In this unusual variant, a graphite cup is inserted into the plasma along an axis parallel to the optical axis of the spectrometer, 11 mm below that axis. The cups are made by drilling a concentric hole into a graphite rod, which is then filled with 50 mg of powder and pressed manually. The other end of the graphite rod is made to fit an alumina rod that slides along a notch, and a magnetic stopper is used to ensure reproducible positioning of the cup in the plasma. The method of carrier distillation was used for the analysis of trace impurities in uranium oxide, with detection limits in the range of 0.02 to 5 µg/g and relative standard deviations of 4 to 12 %. Here, the carrier was a mixture of AgCl and NaF (5+3, m/m), and a 2% concentration of the carrier was used for the analyses.

McCleod et al. [39] reported the successful application of DSI to the simultaneous determination of volatile trace elements in nickel base alloys, using a device built around a car aerial. A sample insertion probe composed of a graphite cup and some connecting graphite and PTFE adaptors was mounted onto an electrically operated car aerial, a variable output dc power supply was used to control the rate of probe elevation and a mechanical stop was used to define the final insertion depth of the probe in the plasma. The major aims of this study were to determine whether probe temperatures were sufficient to melt nickel alloy chips and vaporize volatile elements, and whether calibration curves constructed from aqueous multielement solutions were appropriate for the analysis of these alloy chips. These authors established that aqueous multielement standard solutions (non matrix matched) could be used for calibration. They reported that although significant differences were noted in the emission-time characteristics for the Ni base and solution samples, good proportionality between analyte mass and the integrated emission response enable the use of aqueous standards in calibration. The limits of detection reported for the volatile elements Cd, Mg, Pb and Zn, based on a 5 mg sample were 0.004-0.08 µg/g and precision at the µg/g level was in the range 6-14% RSD.

Sing and Salin [40] published a report on the application of a wire loop direct sample insertion device for inductively coupled plasma mass spectrometry early after the commercial introduction of the then Sciex ELAN. The univariate optimization of a number of operating parameters was performed for manganese : plasma distance from the sampling orifice, insertion depth, plasma power, auxilliary gas flow rate and ion optics settings. The DSI results showed an improvement of 40 over conventional nebulization data, and the linear dynamic range appeared to be 4 orders of magnitude.

One of the major difficulties with ICP-MS when using conventional nebulization is the significant background levels caused by the formation of oxides due to the presence of water vapor. With DSI, the sample was desolvated well before its introduction into the plasma and the background spectrum was therefore greatly simplified and spectral interference problems markedly reduced.

In the first paper from Horlick's group since the initial report on DSI by Salin and Horlick, Pettit and Horlick [34] reported a pneumatically activated system that could sequentially and automatically insert up to 24 probes in a continuously running ICP. For this work, a photodiode array (PDA) spectrometer was used to measure emission time profiles in a 55 nm window, from 211 nm to 266 nm, divided in 1024 pixels. The array was clocked at 12.8 kHz, and its integration time ranged from 80 ms to 5.5 min, which was enough to adequately record the signals of all the elements studied. This system also incorporated a torch of larger diameter than that of more conventional torches, so that larger cups could be inserted into the plasma. However, the only size of graphite cup that was used on this system was a 1/4 in. diameter necked crater electrode, and the effect of increasing the cup's diameter is not discussed.

With this system, Pettit and Horlick investigated the effect of adding a small concentration of oxygen to the normal Ar coolant gas. They found that oxygen tends to enhance the signals and speed up the emission temporal behavior, in fact for Cd, In and Zn a 6% O_2/Ar coolant composition resulted in signals that were too fast to resolve with the PDA spectrometer. Although longer lasting, the signal of Mn was also improved by the addition of oxygen to the coolant gas, for Ni however the signal was not significantly enhanced. The authors proposed that the long vaporization time of Ni could be explained by the formation of a refractory carbide, and they found that the vaporization behavior of Ni could be significantly improved by switching to metal cups. The eventual goal of many DSI investigations is the direct analysis of solids, and results for the direct determination of Zn in six NIST SRM are also reported in this paper.

Shao and Horlick [23] published a report on a mechanical system that could be readily attached to a commercial ICP spectrometer, the ARL 34000 in this instance, with no other modification than the removal of the standard torch and spray chamber. These authors report a volatilization sequence for fifteen elements, with solution samples, that is very similar to that observed in dc arc spectroscopy. They report that the emission time profile is also dependent on the cup size, with sharper peaks observed for smaller-diameter cups, which they propose may simply be due to the more rapid heating of the smaller cups. In this perspective, it is surprising that they also found that plasma forward power had little effect on the emission time behavior. The cup size also affects the precision of the measurements, and intermediate cup diameters were optimal in terms of percent RSD, and also resulted in the best detection limits for many elements.

Linear calibration curves were established for twelve volatile elements (As,Cd,Cu,In,Li,Mg,Mn,Na,Pb,Sb,Sn,Zn) with 10 υL volumes of solutions, and it was found that the signals for these elements were comparatively insensitive to power changes. On the other hand, the signals of Cr and Fe showed marked power dependence, but their calibration curves were linear at both power settings used (1.2 and 1.5 kW). Other elements such as B,Ca,Mo,Ni,V and Zr, which are in general difficult to volatilize and/or are strong carbide formers, had nonlinear calibration curves. Most of the volatile elements had absolute detection limits in the subnanogram range, with an average RSD of 3.3%. The accuracy of the method was evaluated by analyzing digested NBS pine needle SRM, and was found adequate at 13% for a single 10 υL insertion. This method was then extended to the direct determination of nine volatile elements in dc arc powdered standards, the Spex G-standards, Spex TS-6 silicon dioxide base standards, and Spex TS-6 aluminium oxide base standards, with promising results. Linear calibration curves were obtained with the three sets of standards, and furthermore it was found that the matrix (graphite, SiO_2, Al_2O_3) had little effect on these curves.

The next year, Brenner et al. [41] published a sobering report on the trace element analysis of geological materials by DSI-ICP-AES with a graphite cup. These authors documented some interferences that can occur when a graphite cup containing a silicate sample is inserted horizontally into a low-power inductively coupled plasma. First, it is noted that the horizontal insertion of a rod in the plasma resulted in a significant decrease of the Sc(II)/Sc(I) intensity ratio in the normal analytical zone. This marked decrease of the ion to atom ratio could result from a sharp decrease in plasma temperature above the rod, due to heat transfer to the graphite cup or to the disturbance of the plasma's geometry and gas flows. In addition to the thermal disruption of the plasma by the physical presence of the probe, there are chemical reactions that can occur in the plasma and in the cup itself in the presence of such a massive concentration of matrix constituents. Thus, it is reported that at low plasma power the formation of a refractory glassy globule by silicate materials results in delayed volatilization, low intensity multiple peaks, and pronounced tailing. However, in the presence of a graphite diluent, glass formation is prevented and the volatilization rates for copper and zinc increased sharply, as evidenced by early volatilization, improved SBR, and reduced tailing.

The horizontal design of this DSID virtually precludes the optimization of the insertion sequence, so these authors limited their optimization of operating conditions to that of plasma power. They found that at higher power settings the temperature of the probe is apparently elevated, and a more rapid decomposition of the sample ensues, with significantly enhanced signal to background ratios for the two elements studied, copper and zinc. However, it is also reported that for copper an initial erratic vaporization event is still followed by a well pronounced tailing effect at a power level of 2.0 kW, the highest power level on most commercial RF generators for ICP. This paper also reports a multielement volatilization sequence for a group of volatile and refractory elements that is reminiscent of that described by Boumans and Maessen [42] for the dc carbon arc plasma in argon, but which differs slightly from that of Shao and Horlick [23]. Brenner et al. [41]

concluded their study by observing that volatilization of the very volatile elements is faster from the synthetic matrix than from the silicate under identical ICP operating conditions, and that because of these volatilization differences, synthetic salts and oxides cannot be used as calibration standards for the analysis of silicate materials. Furthermore, when samples of standard reference silicate materials (1 part sample + 5 parts graphite) were employed for multielement calibration, poor fits were obtained and their estimate for the accuracy of an analysis based on these curves was +/- 25%.

On the other hand, the next year Broekaert et al. [21] published an optimistic report on the use of direct sample insertion into a nitrogen-argon inductively coupled plasma for the analysis of trace elements in aluminium oxide [21] and in high-purity aluminium [43]. The geometry of the probe, the gas flows, the power level, and other ICP parameters were optimized with dry solution residues. It was found that the difference between net line intensities obtained for cups with and without cover was small, but that the background intensities differed considerably. The background intensity at 213.8 nm and 324.7 nm decreased by factors of 1.3 and 2.3 respectively, when a graphite cover was used on the graphite cups, yet the background intensity at 407.8 nm increased by a factor of 1.3. Thus, the choice between using covers and not using them is very dependent on the particulars of the analytical problem at hand. Smaller cups were again preferred, because they were found to result in steeper heating rates and higher final cup temperatures. A temperature estimate of 3000 K for the smallest cup used in these experiments is inferred from the observation that a strip of tantalum (m.p. 2996 K) melted completely in 15 s when it was carried into a 3 kW nitrogen-argon plasma with this cup.

That year, Hall et al. [44] compared the relative merits of two methods of sample introduction in inductively coupled plasma mass spectrometry : electrothermal vaporization (ETV) and direct sample insertion. The direct sample insertion device used for this work was the wire loop DSID of Sing and Salin [29,30,40] with in situ drying of the samples. Both techniques were found to enjoy common advantages over pneumatic nebulization; these include a low sample volume requirement, higher sensitivity and reduced oxide and hydroxide isobaric interferences.

By comparison, the wire loop DSI device was simpler in design and less expensive to construct than its ETV counterpart. The duration of the peaks was much shorter, generally by a factor of 2-10, hence peak heights obtained by DSI were significantly greater than those obtained by ETV. With DSI, the entire sample is presented for vaporization whereas the transport efficiency by ETV introduction was generally of the order of 60-80%. Indeed, a general absence of transport problems was highlighted as a major advantage of DSI. However, these authors felt that although better precision and detection limits may be anticipated using DSI in the analysis of relatively "clean" and dilute solutions, the ETV technique has greater flexibility in providing accurate analysis of more complex solutions that contain high concentrations of total dissolved salts.

Reisch et al. [45] published a report on volatilization studies for Fe and Cd in their direct determination by inductively coupled plasma emission spectrometry using direct sample insertion and external electrothermal evaporation of powders the next year. The object of this work was to study the evaporation and excitation processes. The evaporation rates were monitored by using ^{59}Fe and ^{115}Cd radioactive isotopes, and the influence of various parameters such as the probe's geometry, carrier gas injection and flow rates were investigated. The performance of the system was characterized for powdered graphite and ceramic matrices, and it was found that a special feature of electrothermal vaporization is that both the heating time and temperature can be controlled whereas in direct sample insertion only the duration of the insertion can be selected.

It was found that the volatilization of Fe, in particular, depended considerably on the use of an additive. This was confirmed by the studies with ^{59}Fe, where it was found that Fe could be almost completely volatilized from a graphite matrix within 10 s by direct sample insertion when thermochemical additives were used. With ceramic matrices, the volatilization efficiency was usually better than 90%. On the other hand, the studies with Cd at the same time clearly showed that the addition of a thermochemical reagent led to a decrease of the excitation efficiency and thus were disadvantageous in the case of very volatile elements.

Umemoto and Kubota [24,46] have published two reports on their efforts to improve the detection limits of DSI for the determination of trace levels of elements that are difficult to determine by the conventional nebulizer methods without preconcentration. Their first paper [46] deals with the determination of As and Sb in iron and steel by direct insertion into an ICP, with a graphite cup probe. The sensitivity of ICP-AES is considerably less for these two elements than for most alkaline earth and transition elements, and it is difficult to determine them accurately at trace concentrations, hence these author's interest in lowering the technique's detection limits. The authors postulated that a shallow cup with a small opening would be the most advantageous probe geometry, and settled on a cup with a 3.5 mm deep well, an inner diameter of 3.0 mm and walls 0.2 mm thick. They then proceeded to optimize three operating conditions, insertion depth, RF power, and observation height. They found that a deep insertion, about 6 mm above the load coil, with an intermediate power setting, 1.6 kW, and a fairly standard observation height, between 14 and 16 mm above the load coil, provided the best signal profiles. They found that higher power settings resulted in sharper peaks, but the increased peak height did not reflect itself in an improvement of SBR. In contrast to Haraguchi's findings [12], these authors reported that no remarkable effect on the determination of arsenic and antimony was observed for an acid concentration range between 0.5 and 2.5 M of either HNO_3 or H_2SO_4. However, these authors reported a suppression of the signals of As and Sb, by as much as 28%, at Fe concentrations above 1 mg/ml. Finally, the calibration curves obtained with 25 µL of standard solutions were linear up to 10 µg/mL for As and 5 µg/mL for Sb, and their absolute detection limits were 1.1 ng and 0.2 ng respectively.

The second paper by Umemoto and Kubota [24] followed much the same line of thought, and sought to improve detection limits by optimizing each aspect of the insertion sequence. In particular, the aspects covered by this study included the effect of the thickness of the probe's walls on the signal's peak height and on background intensity, the relation between cup volume, sample volume and emission intensity, as well as the usual optimization of insertion depth, rf power and observation height. They found that for all the elements studied but Pb, the thinner cups resulted in sharper, more intense peaks. Thus, a cup of 0.2 mm thickness resulted in the highest emission intensity, but the background intensity was highest for this cup thickness. Unfortunately, the authors did not use SBR as their optimization criterion, rather they struck a middle ground between the difficulty of preparing cups with very thin walls and the risk of memory effects presented by thicker walls, and settled on an intermediate wall thickness of 0.5 mm. The detection limits for the nine elements studied (As,Bi,Cd,Cu,Fe,Ni,Pb,Sb,Sn) for the most part fell below 1 ng/mL, and in particular the detection limits for As and Sb fell below their previous estimate by roughly an order of magnitude.

A milestone in the development of DSI was the publication of two series of articles by Karanassios and Horlick. In the first [36,47,48], they described the design of a direct sample insertion device for ICP-MS. This DSI device was developed to fit onto a commercial ICP-MS instrument, the Perkin-Elmer/SCIEX Elan, where the plasma is operated horizontally. It is easier to use gravity, rather than fight it, when loading the graphite cups with sample. The authors describe a mechanical system that moves smoothly from a vertical load position to a horizontal insertion position [36].

Another important section is the one on data acquisition considerations. Because the signals are transient, they must be acquired and digitized in real time in DSI-ICP-MS as they are in DSI-ICP-AES. The Elan was thus used in the peak hopping mode to keep some multielement measurement capability. Unfortunately, the software overhead imposed by the Elan system did not permit data acquisition rates that were high enough for DSI applications. However, the authors were quick to point out that this is not an intractable problem, nor one that is unique to DSI-ICP-MS [36].

In the second publication on DSI-ICP-MS [47], an extensive set of background spectra were presented. These included spectra of the plasma only and background spectra for DSI probes such as graphite, Mo and Ta cups as well as a W wire loop. The elimination of water in DSI systems resulted in a significant reduction of numerous background species, particularly those containing oxygen and hydrogen. In general, the sample carrying probes did not introduce significant background spectral features. The insertion of cups made from graphite, Mo, Ta and W resulted only in low intensities for the corresponding elements.

The elimination of some spectral interferences and matrix effects in inductively coupled plasma mass spectrometry was discussed in the third publication of the series on DSI-ICP-MS [48]. Isobaric interferences from analyte and matrix based molecular ions, particularly oxide species, are a nagging problem in ICP-MS. The absence of water in DSI systems was used to eliminate some of these problems. Examples are shown for BaO^+, CeO^+ and ClO^+ which are reduced to very low levels (ca. 0.1%). Another problem of ICP-MS is a non-spectroscopic matrix effect whereby an excess of an element, particularly heavier elements, suppresses the signal of lighter elements. By relying on differential thermal volatilization, the appearance of U was retarded and its suppressive matrix effect on Zn thus alleviated.

In their second series [49,25,50], Karanassios and Horlick did much the same for DSI-ICP-AES. The first of the three reports described a computer controlled device which was an extension of the design previously described by Pettit and Horlick [34]. The sample carrying probes can either be graphite cups, metal cups or wire loops, and the system is further automated by the use of a carousel capable of holding up to 24 probe assemblies. This report included a detailed discussion of the data acquisition requirements imposed by the transient spectral signals resulting from this sample introduction system. A measurement system was described that is capable of digitizing, in real time, the complete transient spectral signal simultaneously from four channels of a direct reading polychromator.

A characterization of the direct insertion device followed [25], where the emission time behavior for several elements with a range of volatilization properties was characterized as a function of probe geometry, composition, insertion speed and position as well as applied RF power. This report particularly emphasized the importance of a rapid but controlled insertion of the sample probe assembly. It also was found that probe design is very important and that long undercut graphite cups provide best results. Graphite was deemed the best all round probe material, although it has the disadvantage of resulting in the formation of refractory carbides with many elements.

The last of the three publications [50] dealt with the application of chemical modification in direct sample insertion inductively coupled plasma atomic emission spectrometry. With a graphite cup based system, poor results are obtained for refractory and carbide forming elements, such as Al, B, Ca, Sr and Zr. The volatilization enhancing properties of four thermochemical additives (KCl, KF, NaCl and NaF) were studied in order to improve the vaporization characteristics of this class of elements.

Approximately equivalent enhancements in sensitivity were observed with KF and NaF. However, a problem emerged with KF in that a high volatilization rate was observed during the initial stages of the insertion, and the plasma was frequently extinguished.

Chan and Horlick [51] published a report on an automated direct sample insertion device where graphite cups can be mechanically inserted into the plasma, and the sequence is completely under computer control via a stepper motor. This time, multichannel high-speed electronics were developed for a direct reading polychromator that allowed the real-time digitization of the transient spectral signals from up to six channels simultaneously. A further step toward full automation was taken by using a small robot arm to exchange the sample probes. Once more, the selling point of DSI for AES is that it provides MS caliber detection limits in the pg range for volatile elements like Cu and Zn.

For their next publication, Chan and Horlick [52] studied some signal characteristics in direct sample insertion inductively coupled plasma atomic emission spectrometry. It was found that the basic temporal behavior of the emission signals strongly depended on the method of sample treatment and the sample matrix. These authors emphasized that it was necessary to standardize the treatment of the standards and samples, in order to obtain consistent results. Unfortunately, the sample treatment requirements of some elements are to some extent incompatible, and the best sample treatment for each analyte must still be determined empirically. It was also found that the geometry and composition of the sample probe, the speed and depth of insertion, as well as the applied RF power all affect the signal's temporal behavior.

The most recent publication on DSI is a contribution by Umemoto and Kubota [53] who report a detailed comparison between some characteristics of the inductively coupled plasma with graphite cup sample introduction and with pneumatic nebulization. With DSI, the core of the plasma had a toroidal shape, and its linear dynamic range was roughly four orders of magnitude, which is slightly smaller than with pneumatic nebulization. It was also found that the plasma did not have two distinct thermal and non-thermal excitation zones, in contrast to nebulization plasmas. The influence of the graphite cup's geometry and its position in the plasma on background intensity and the intensity ratios of ionic to atomic lines for four elements (Cd, Cu, Pb & Zn) was also studied. It was found that the ratios for Cd and Zn are significantly affected by the cup position.

DIRECT ANALYSIS OF SOLIDS

Solid samples still pose a difficult challenge to analysts in activities such as geochemical exploration, mining and metallurgy, and pollution monitoring. Indeed, the latest innovations in instrumentation have not had as significant an impact in these fields as in many other applications of analytical chemistry, because these new techniques still rely on the prior dissolution of the samples. In most cases, the sample dissolution process is much more time consuming than the subsequent instrumental determination, owing to the resistance of matrix components to chemical decomposition. In practical terms, this means that up to three days can be spent on the preparation of sample solutions before a typical geochemical assay is completed [54].

It is thus worthwhile to investigate whether useful results could be obtained by techniques designed to directly analyze solids like rocks, ashes, sediments and various mineral samples [55]. To date however, only four methods for the analysis of solid samples have received some measure of commercial acceptance, Neutron Activation Analysis, X-Ray Fluorescence (XRF), and both Arc and Spark Atomic Emission Spectrometry. In the last twenty years, considerable research activity has gone into the development of techniques for the direct trace analysis of solids by Atomic Absorption Spectroscopy (AAS) [56,57,58]. Yet none of the proposed methods has managed to gain acceptance as an assay technique in the fields that routinely deal with solid samples. It has been suggested [55] that three factors contribute to undermine the usefulness of these methods, first and foremost that they are often impractical and require complicated instrumentation, next that they suffer from poor precision and that there are difficulties with their standardization.

Since its introduction as an atomic spectroscopy source, the inductively coupled plasma has generated an upsurge of interest for the direct analysis of solids by atomic emission spectrometry [2,4,55]. In particular, the direct insertion of solid samples in the ICP promises to overcome many of the limitations of the earlier atomic spectroscopy techniques. This section will outline the various approaches that have been devised for the direct trace elemental analysis of solid samples by inductively coupled plasma. Throughout this survey, the forte and the shortcomings of each approach will be examined, to help in the formulation of a set of criteria by which to evaluate the results that will be presented later in the thesis. Out of the many reports published on each method, only those that best highlight their unique features are reviewed, for the sake of clarity.

DRY POWDER ENTRAINMENT

A number of proposals have been made for the direct introduction of powders in the plasma. In an early instance, Dagnall et al. [59] compared the performance of a swirl cup and a fluidized bed chamber to entrain powders into an argon carrier gas flow. The fluidized bed proved superior by reducing powder surges. In this device, powdered samples were placed on a sintered disc through which argon was flowed. A similar approach was used recently by Guevremont and de Silva [60,61] for the direct determination of several elements in silica, silica-immobilized 8-hydroxyquinoline, and Chelex-100. Here, an arm driven by a solenoid was used to vibrate a glass container through which a stream of argon flowed. The vibration of the container suspends the solid particles in the gas flow, which is then routed to the plasma. Although the mechanical motion of the container reduced the importance of particle size on the transport process, it remains a deciding factor in the performance of the system.

In another attempt at introducing powders into an ICP, Hoare and Mostyn [62] placed powdered solid samples into a borosilicate cup at the base of a plasma torch. The cup was then mechanically vibrated and a low argon flow rate through the vibrating powder carried the solid into the plasma. They found that the details of the powder preparation procedure have a drastic effect on the reproducibility of the technique's performance, and that the preparation of the standards should be closely matched to that of the samples. Thus, they concluded that this technique would perform well for qualitative analyses but that its application to quantitative analyses is probably limited. In a similar vein, Ng et al [63] used a miniature unagitated swirl cup to introduce coal fly ash powder into the ICP. Here, it was found that high power levels (2.0 kW) and high observation heights were needed. Thus, it is likely that the coal fly ash particles were slightly oversized and did not undergo complete vaporization in the plasma's hot core.

The acoustic energy from a spark between two electrodes held above a powder has also been used to disperse finely ground solids into a stream of argon, which was then injected into the ICP [64,65]. Scott [64] used a high energy spark to elutriate finely ground geological materials from a vial. This report not only suggested that the acoustic energy of the spark is instrumental in elutriation, but also that the spark may break the particles up to yield smaller particles, or even vaporize the material. However, exponential drop-off of plasma emission intensity occurred over time due of segregation effects arising from the different densities and particle sizes of the powders. More recently, Hu et al. [66] used a low energy but high frequency discharge to blow up powdered samples, and found that the transport efficiency was high (> 80%) for small particles (< 75 μm) of various materials, including silicate ores, carbonate ores, iron ores, and ceramics. The size of the sample was limited to about 70 mg with their device, yet they reported relative standard deviations of the signal intensity on the order of 5%, which is quite low for these types of materials.

In most accounts of continuous dry powder introduction [59,60,61,62,64,65] the signal is found to decay with time, which suggests the preferential entrainment of smaller particles. Optimally, particle sizes should be less than 10 μm to ensure complete vaporization of the particles in the plasma, and carrier gas flows should be kept low [67,68]. However, more often than not, uniformity of particle size cannot be ensured and the start of data acquisition must be closely synchronized with the start of powder injection to achieve acceptable reproducibility [64]. In any case, sample grinding procedures play a dominant role in dry powder injection methods.

Geological materials can generally be ground to appropriate sizes within reasonable time, about 30 minutes [69], using micronising mills. Vegetation samples are usually dried, most often they are lyophilized, and can then be ground to small sizes quite rapidly [54,70], while animal tissue, bones and most foodstuff can be reduced to micron and sub-micron particles within minutes using sonic/cavitation homogenizers [71]. Although these procedures are not trivial and must be carefully optimized, they are simpler and more rapid than the various ashing procedures that are necessary to convert these materials into liquid solutions. Furthermore, most, if not all of these procedures, also require that the sample be ground to some extent to ensure quantitative recovery of the analyte [54,72].

SLURRIES

Attempts have also been made to nebulize solids, suspended in a slurry [73,74,75], into the plasma. In their report on the application of slurries to the analysis of geological materials, Halicz and Brenner [75] suggested that the use of slurries and suspensions combined the advantages of solid and liquid sampling, since the sample could be transported conveniently to the plasma with a high solids nebulizer. However, they also reported that slurry nebulization for ICP-AES with geological materials appears to require that textural, mineralogical, and chemical compositional properties of the samples and standards be common.

Slurries with low concentrations of suspended solids, such as wear metals in oil, can be directly nebulized with pneumatic nebulizers without experiencing serious clogging problems [76]. But when the solid content is higher, above 5% wt/vol, Babington nebulizers must be used. These nebulizers were originally developed for spraying paint and are essentially free from clogging, however, they are also less efficient than pneumatic nebulizers at producing small droplets [1]. Fry and Denton [77] employed a Babington sphere nebulizer to nebulize a slurry of tomato paste and other foodstuffs into a flame, and Mohamed and Fry [71] used a v-groove nebulizer for a suspension of homogenized animal tissue.

Again, particle size effects are dominant, and in general slurry particles must be less than 10 μm in diameter to be quantitatively transported to the source and completely decomposed before leaving the latter's hot core [76,78]. Uniformity of the particle size distribution from sample to sample must be ensured to maintain acceptable precision [75,78], and both the chemical composition and particle size distribution of the standards and samples must be matched to procure accurate results [69]. Thus, Fuller et al. [69] found that standard additions was not applicable to the analysis of geological samples by slurry methods, because the physical properties of the standard and the sample were not matched closely enough. On the other hand, Fry and Denton [77] and Miller-Ihli [79] found that standard additions yielded accurate results for the analysis of animal tissue slurries by ICP and graphite furnace atomic absorption spectrometry proportion of the analyte had been extracted into solution during the preparation of the slurries which, in turn, led to a closer match of the sample and standard.

Among the other factors that must be taken into account in the preparation of slurries are the ability to form and hold the suspension [75,79,80,81,82,83], the composition of the suspension medium [84], and the sample loading [78,85,86]. Ideally, the composition of a slurry should only be dictated by the ability to form and hold a suspension in the medium of choice. However, it has been demonstrated that the ability of the source to completely atomize and excite the analyte is impaired by high sample loadings [78,85]. High levels of solids in suspension affect the delivery rate of the slurry, by altering its viscosity [78], and have been shown to cause a cooling of the plasma [85]. Thus, although suspensions of up to 40% coal have been nebulized into an ICP [86], sample loads of 10% are more commonly used.

ABLATION

The most simple approach to ablation was probably that of Farnsworth and Hieftje [87] who used an arc filament from the plasma itself to vaporize the sample. The arc filament extended from the base of the plasma to a grounded conducting sample, or a non-conducting sample mixed with a conducting support such as metal or graphite powder. With alloys and coal fly ash, the time profile of the signal was so capricious that the quantitative application of this technique was ruled out.

Johnes et al. [88] described a modification of the dc arc for the sampling of solid conducting samples, where an arc was allowed to wander over the sample and the eroded material was carried to a separate excitation source by a gas stream. Dalhquist et al. [89] then used this device as aerosol generator for an ICP. Ohls and Sommer [90] have also reported a similar approach for the analysis of steels and some ground non-conducting materials mixed with copper powder and pressed into a conducting pellet. The erosion of the sample was found to proceed without the selective volatilization of volatile elements [1, 91], thus allowing representative sampling of the materials.

A high voltage spark was used by Human et al. [92] to produce particles from solid conducting materials, which were then transported to a plasma in a gas fed through the spark chamber. Copper was determined in aluminum, iron and brass by this approach. The signal was found to stabilize only after long pre-burn delays on the order of 2 minutes, but eventually achieved a steady state. The reproducibility of the signal was acceptable for solid samples, around 5%, and the detection limits were in the parts per million range. Marks et al [93] and Beaty et al. [94,95,96,97] reported similar applications of sparks as aerosol generators for the analysis of various alloys, which eventually resulted in the commercial development of a technique known as Separate Sampling and Excitation Analysis (SSEA) [98]. Again, long pre-burn times were needed to allow the signal to stabilize, and memory effects were also reported. Precision was excellent, often better than 0.5% RSD, and when internal standards and interelement correction factors were used, accurate analyses of standard reference materials were possible.

Solid conducting aluminum alloys and non-conducting powders pelletized with copper were also analyzed with spark volatilization by Aziz et al. [99]. They used a medium voltage spark to generate an aerosol of the al. [99]. They used a medium voltage spark to generate an aerosol of the samples, which was then swept into a high power Ar/N_2 plasma. Apart from the long pre-burn time necessary to achieve steady signals, these authors also reported that matrix effects in the spark sampling resulted in poorer precision for the mixtures of non-conducting materials. More importantly, they found that the efficiency of ablation was less than that of solution nebulization by two orders of magnitude, and hence that poorer detection limits were obtained with this method than with the conventional acid digestions.

In general, the spark is preferable to the arc as a sampling device [1]. Whereas an arc tends to burn for some time at one or a few spots, which leads to selective and erratic volatilization, a spark strikes many different spots on the sample's surface, which ensures a more representative sampling. Also, since it is not thermal in nature, spark sampling is free from selective volatilization and can handle low melting alloys. However, the spark is not an ideal sampling device. Very little sample is ordinarily consumed during sparking, so that spark methods often have higher limits of detection than their arc counterparts.

A high power, pulsed laser beam is capable of vaporizing solid materials when it is focused on a small diameter spot (5 to 50 μm), even if the sample is not electrically conductive. When the laser radiation strikes the surface, it produces a high-temperature vapor plume of atoms, ions and molecules, which can then be swept by an argon stream into an ICP. Abercrombie et al. [100] used a pulsed transversed excited CO_2 laser with a maximum power of 17 kW to vaporize powdered solid samples, and the resultant aerosol was swept in an argon stream to an inductively coupled plasma. Carr and Horlick [101] used a similar approach with a ruby laser for analyzing aluminum, brass, steel, rock, ceramics and biological materials. They found that the greatest problem with this method was the fluctuation of the laser's power, which adversely affected shot to shot reproducibility.

Thompson et al. [102] used laser ablation to analyze steel samples, and determined that only 1 μg of material was actually vaporized while about 30 μg went into the formation of a crater around the laser spot. As a result, although their absolute detection limits were comparable to those of conventional nebulization, their concentration detection limits were poorer.

ELECTROTHERMAL VAPORIZATION

In the 1960s, L'vov proposed electrothermal vaporization (ETV) as an alternative to flames for atomic absorption spectrometry (AAS), and thus launched graphite furnaces atomic absorption spectrometry (GFAAS) on its remarkably successful career [1]. Since then, electrothermal vaporization has also been used for the direct analysis of solids. Fittingly, L'vov [103] was the first to outline the analysis of solid samples by ETV-AAS in a paper on applications of graphite furnaces as atomizers. Since then, ETV-AAS has successfully been used for the direct analysis of some types of solid samples, mainly highly organic materials and others with a relatively simple matrix. In all cases, electrothermal vaporization works best for samples where the matrix and analyte have widely different volatilities [55].

Electrothermal vaporization has also been used to generate sample aerosols for other sources, such as flames, microwave induced plasmas (MIP), and ICP. Ng and Caruso [104] have published a review of the applications of ETV as a sampling device for atomic emission, and they found that many of the limitations of electrothermal atomic absorption spectrometry are alleviated by the separation of the sampling of solids from the atomization and excitation of the analyte. In one instance, Gunn et al. [105] vaporized samples from a resistively heated graphite rod under a glass dome. They found that this device was applicable to about 20 elements, but that poor detection limits were obtained for carbide forming elements such as Zr, Mo, and Cr. With this problem in mind Kirkbright and Snook [106] employed a 0.1% mixture of trifluoromethane (freon 23) in argon as the carrier gas. Detection limits for the carbide forming elements were improved by one or two orders of magnitude compared to argon alone. In similar experiments Hull and Horlick [107] determined up to 27 elements. They noted that high levels of sodium caused a spatial shift of the emission profile of many elements, but that the integrated intensity was not affected.

Park and Hall used electrothermal vaporization for the analysis of geological materials by ICP-MS [108,109]. The determination of Mo and W down to 0.03 µg/g and 0.06 µg/g respectively was done by the method of isotope dilution [108]. It was found that electrothermal vaporization eliminated the need for the laborious, time consuming separation steps associated with sample introduction by conventional nebulization. Memory effects were evident in the determination of W due to carbide formation during ashing, in spite of the presence of Freon gas during vaporization.

In the second publication [109], the determination of Tl by isotope dilution ETV-ICP-MS in aqueous solutions of geological materials obtained following the commonly employed "total" mixed acid attack was reported to be efficient and accurate. Sample introduction by ETV rather than by conventional nebulization was found to permit the direct determination of Tl in solutions which contain about 1% dissolved salts, and avoid salt deposition on the sampling orifice.

As a rule, the operating conditions of the plasma are very similar to those used with conventional sample introduction devices, in terms of gas flows, applied power levels, and viewing height. In one report [95] on the application of ETV to liquid samples, it is found that the optimal power levels are lower than with solution nebulization, presumably because the sample is already desolvated and partially atomized by the sample introduction device. The principal parameters that must be optimized with ETV sample introduction are the volume of the vaporization cell and the length of connecting tubing [105,110], the temperature and the heating rate of the vaporizer [111,112], and the porosity of the ETV support. Apart from the volume of the vaporizer chamber, its geometry can also have an important impact on throughput, as some analyte may be lost by adsorption onto the walls of the chamber [111,113,114].

CHEMICAL VAPOUR GENERATION

To many chemists, atomic spectroscopy seems closer to physics or engineering than it does to their area of activity, probably because this discipline does not emphasize the use of chemical reactions in its procedures but relies mostly on instrumental alternatives. Yet, chemical modification of the analyte is an integral part of the atomic spectroscopist's arsenal. It has been used by arc spectroscopists to enhance the volatility of refractory elements, and to either prevent the formation of refractory carbides with the graphite electrode's body or to break these carbides down [42,115]. It has also been used in atomic absorption to introduce samples into a flame in the gaseous state, by converting the elements to a chemical form that is volatile at or near room temperature [1]. Elements such as As and Se are easily converted in solution to hydrides that can then be swept out of solution and into the atomizer. The ready reaction of As, Bi, Ge, Pb, Sb, Se, Sn, and Te with $NaBH_4$ in acidic solutions to form volatile hydrides has long been used in AAS, and has also been used as a sample insertion procedure in ICP-AES. Thompson et al. [116,117] reported the first successful coupling of hydride generation techniques with ICP-AES. Since then, the application of hydride generation has been reported for the determination of Se [118] and As, Bi, and Sb in various geological samples [119] and in vegetation samples [118].

The reaction of some metal ions with appropriate complexing agents produces volatile metal complexes. For example, Be, Cu, Cr, and Fe form volatile trifluoroacetonates [1], which can then be introduced directly into the atomization source. Along similar lines, Skogerboe et al. [120] used a chloride generator to volatilize metals from residues as volatile chlorides into an atomic absorption flame or microwave plasma according to the following reaction :

$$Me_nY_m\ (s) + HCl_{excess}\ (g)\ \text{-[heat]->}\ MeCl_n\ (g) + H_mY$$

The system could be used at temperatures up to 1000°C and hence was applicable to about 30 elements which form volatile chlorides with boiling points below this value.

Furthermore, both electrothermal volatilization and direct sample insertion benefit from the application of thermochemical reactions that enhance the volatility of some elements [121,10,45]. The work of Kirkbright and Snook [121] who employed a 0.1% mixture of trifluoromethane

(Freon 23) in argon to enhance the volatility of some carbide forming elements in graphite rod ETV has already been discussed in the last section.

HORIZON TECHNIQUES

A recent publication by Goldberg [122] suggested that the atom vapors generated by imploding thin film plasmas be swept into an inductively coupled or microwave induced plasma. Exploding and imploding thin film plasmas are well characterized [122,123,124,125,126] and it has been shown that their mass flow characteristics can be tailored by the design of their electrical circuit [123]. These new atom cells have shown great promise for the vaporization of refractory materials [122,127], but high spectral background levels and self-absorption interferences make them inferior spectroscopic sources [122,123,124,125,126].

Clark [127] has reported the determination of trace metals in powder micro samples using exploding thin film atomization and excitation. Duchane and Sacks [128,129] have reported detection limits in the low to sub-ng range for 14 trace elements by the atomic emission determination in micro samples with exploding thin-film excitation.

Theta pinch discharges are also establishing themselves as powerful vaporizers for refractory solids [130], and are likely to be coupled to other emission sources in the near future. These sources are well characterized [131,132,133] and can be precisely and reproducibly controlled by tuning a few components of their electrical circuits [133]. In their publication on the sampling and excitation of refractory solids with a theta pinch discharge designed as an atomic emission source, White and Scheeline [130] report the application of this atom cell to the analysis of tungsten powder, boron nitride and aluminum oxide ceramics. However, in a more recent publication Scheeline et al. [134] discuss some complications to the use of theta-pinch discharges for quantitative analyses. They found that changes observed in emission time behavior can be attributed to the effects of particle size and apparent nonrepresentative sampling, as well as to line reversal.

DIRECT SAMPLE INSERTION

Salin and Horlick's first report on DSI already demonstrated the potential of DSI for the analysis of powders [7]. Since then, various reports on solid analyses by DSI have been published for Ni base alloys [39], coals [34], botanicals [34], powdered arc standards [23], and aluminum oxide [21,43]. The results presented in each were encouraging, with promises of low detection limits, good precision and accuracy, and shorter analysis time. However, these materials all had simple matrices that did not significantly affect the plasma not the thermochemical reactions responsible for the vaporization of the analytes. The optimal performance characteristics of DSI had thus been established, whether it would survive the harsh test of real samples remained to be verified.

The report by Brenner et al. [41] at the Geological Survey of Israel suggested that the more complicated matrices of naturally occurring materials ruled out their analysis by DSI. This dismissal of DSI seemed peremptory, and the development of a DSI method for the analysis of sediment was undertaken. Two motivating factors stand behind this work, one is practical and the other academic. The Ontario Ministry of the Environment believed that DSI could be developed into a routine method for the routine analysis of environmental samples such as soils, sediments and botanicals. As spectroscopists, we sought to push the ICP to its limits and see whether it deserved to be called the ideal atomic emission source.

This thesis will describe the design and implementation of a method for the direct determination of some elements in sediment matrices by their insertion as pellets into the inductively coupled plasma. Although the bulk of the work reported herein has been carried out on an atomic emission instrument (ICP-AES), there is some indication that similar strategies could be advantageously implemented on the increasingly popular mass spectrometry (ICP-MS) systems.

REFERENCES

1)- J.D. Ingle Jr and S.R. Crouch, *Spectrochemical Analysis*, Prentice Hall, New Jersey, 1988

2)- A. Montaser and D.W. Golightly, Ed.; *Inductively Coupled Plasmas in Atomic Spectrometry*, VCH, New York, 1987

3)- P.W.J.M. Boumans, Ed.; *Inductively Coupled Plasma Emission Spectroscopy - Part 1 : Methodology, Instrumentation, and Performance*, Chemical Analysis series vol. 90, John Wiley and Sons, Inc: New York (1987)

4)- P.W.J.M. Boumans, Ed.; *Inductively Coupled Plasma Emission Spectroscopy - Part 2 : Applications and Fundamentals*, Chemical Analysis series vol. 90, John Wiley and Sons, Inc: New York (1987)

5)- A.T. Zander, *Anal. Chem.* **58**, 1139A (1986)

6)- D. Sommer and K. Ohls, *Fresenius Z. Anal. Chem.* **97**, 304 (1980)

7)- E.D. Salin and G. Horlick, *Anal. Chem.* **51**, 2284 (1979)

8)- V. Karanassios and G. Horlick, *Spectrochim. Acta Rev.* **13**, 89 (1990)

9)- G.F. Kirkbright and S.J. Walton, *Analyst* **106**, 276 (1982)

10)- G.F. Kirkbright and Z. Li-Xing, *Analyst* **106**, 617 (1982)

11)- H. Haraguchi, M. Abdullah, T. Hasegawa, M. Kurosawa and K. Fuwa, *Bull. Chem. Soc. Jap.* **57**, 1839 (1984)

12)- M. Abdullah, K. Fuwa and H. Haraguchi, *Spectrochim. Acta* **39B**, 1129 (1984)

13)- E.R. Prack and G.J. Bastiaans, *Anal. Chem.* **55**, 1654 (1983)

14)- M. Muller-Vonmoos, G. Kahr and A. Rub, *Thermochim. Acta* **20**, 387 (1977)

15)- D.J. Morgan, *Therm. Anal.* **12**, 245 (1977)

16)- E.K. Gibson, *Thermochim. Acta* **5**, 243 (1973)

17)- H.K. Friedman, *Thermochim. Acta* **1**, 199 (1970)

18)- P.K. Gallagher, *Thermochim. Acta* **41**, 323 (1980)

19)- A.G. Page, K.H. Madraswala, S.V. Godbole, M.J. Kulkarni, V.S. Mallapurkar and B.D. Joshi, *Frezenius Z. Anal. Chem.* **315**, 38 (1983)

20)- A.G. Page, S.V. Godbole, K.H. Madraswala, M.J. Kulkarni, V.S. Mallapurkar and B.D. Joshi, *Spectrochim. Acta* **39B**, 551 (1984)

21)- G. Zaray, J.A.C. Broekaert and F. Leis, *Spectrochim. Acta* **43B**, 241 (1988)

22)- N.W. Barnett, M.J. Cope, J.F. Kirkbright and A.A.H. Taobi, *Spectrochim. Acta* **39B**, 343 (1984)

23)- Y. Shao and G. Horlick, *Appl. Spectrosc.* **40**, 386 (1986)

24)- M. Umemoto and M. Kubota, *Spectrochim. Acta* **44B**, 713 (1989)

25)- V. Karanassios and G. Horlick, *Spectrochim. Acta* **45B**, 104 (1990)

26)- E.D. Salin and M.M. Habib, *Anal. Chem.* **56**, 1186 (1984)

27)- M.M. Habib and E.D. Salin, *Anal. Chem.* **57**, 2055 (1985)

28)- M. Abdullah, K. Fuwa and H. Haraguchi, *Appl. Spectrosc.* **41**, 715 (1987)

29)- E.D. Salin and R.L.A. Sing, *Anal. Chem.* **56**, 2596 (1984)

30)- R.L.A. Sing and E.D. Salin, *Anal. Chem.* **61**, 163 (1989)

31)- C.V. Monasterios, A.M. Jones and E.D. Salin, *Anal. Chem.* **58**, 780 (1986)

32)- Z. Li-Xing, G.F. Kirkbright, M.J. Cope and J.M. Watson, *Appl. Spectrosc.* **37**, 250 (1983)

33)- M. Abdullah and H. Haraguchi, *Anal. Chem.* **57**, 2059 (1985)

34)- W.E. Pettit and G. Horlick, *Spectrochim. Acta* **41B**, 699 (1986)

35)- V. Karanassios and G. Horlick, *Appl. Spectrosc.* **41**, 360 (1987)

36)- V. Karanassios and G. Horlick, *Spectrochim. Acta* **44B**, 1345 (1989)

37)- R.L.A. Sing, Ph.D. Dissertation, McGill University, 1986

38)- A. Lorber and Z. Goldbart, *Analyst* **109**, 155 (1985)

39)- C.W. McCleod, P.A. Clarke and D.J. Mowthorpe, *Spectrochim. Acta* **41B**, 63 (1986)

40)- R.L.A. Sing and E.D. Salin, *Anal. Chem.* **58**, 975 (1986)

41)- I.B. Brenner, A. Lorber and Z. Goldbart, *Spectrochim. Acta* **42B**, 219 (1987)

42)- P.W.J.M. Boumans and F.J.M.J. Maessen, *Spectrochim. Acta* **24B**, 585 (1969)

43)- G. Zaray, P. Burba, J.A.C. Broekaert and F. Leis, *Spectrochim. Acta* **43B**, 255 (1988)

44)- G.E.M. Hall, J.C. Pelchat, D.W. Boomer and M. Powell, *J. Anal. At. Spectrosc.* 3, 791 (1988)

45)- M. Reisch, H. Nickel and M. Mazurkiewicz, *Spectrochim. Acta* **44B**, 307 (1989)

46)- M. Umemoto and M. Kubota, *Spectrochim. Acta* **42B**, 491 (1987)

47)- V. Karanassios and G. Horlick, *Spectrochim. Acta* **44B**, 1361 (1989)

48)- V. Karanassios and G. Horlick, *Spectrochim. Acta* **44B**, 1387 (1989)

49)- V. Karanassios and G. Horlick, *Spectrochim. Acta* **45B**, 85 (1990)

50)- V. Karanassios, M. Abdullah and G. Horlick, *Spectrochim. Acta* **45B**, 118 (1990)

51)- W.T. Chan and G. Horlick, *Appl. Spectrosc.* **44**, 380 (1990)

52)- W.T. Chan and G. Horlick, *Appl. Spectrosc.* **44**, 525 (1990)

53)- M. Umemoto and M. Kubota, *Spectrochim. Acta* **46B**, 1275 (1991)

54)- HASL-300, EML Procedures Manual, J.H. Harley ed., Environmental Measurements Laboratory, U.S. Department of Energy, 1972, originally issued in 1957 as NYO-4700

55)- J.C. Van Loon, *Anal. Chem.* **52**, 955A (1980)

56)- F.J. Langmyhr, *Analyst* **104**, 993 (1976)

57)- D.J. Koop, M.D. Silvester and J.C. Van Loon, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1975, Cleveland, Ohio

58)- T. Kantor, E. Pungor, J. Szatisz and L. Bezur, *Talanta* **26**, 357 (1979)

59)- R.M. Dagnall, D.J. Smith, T.S. West and S. Greenfield, *Anal. Chim. Acta* **54**, 397 (1971)

60)- R. Guevremont and K.N. de Silva, *Spectrochim. Acta* **41B**, 865 (1986)

61)- R. Guevremont and K.N. de Silva, *Spectrochim. Acta* **41B**, 875 (1986)

62)- R.C. Hoare and R.A. Mostyn, *Anal. Chem.* **39**, 1153 (1967)

63)- K.C. Ng, M. Zerezghi and J.A. Caruso, *Anal. Chem.* **56**, 417 (1984)

64)- R.H. Scott, *Spectrochim. Acta* **33B**, 122 (1978)

65)- H. Benli, *Spectrochim. Acta* **38B**, 81 (1983)

66)- Weifan Hu et al., *Fenxi Huaxue* **9**, 466 (1981)

67)- G.M. Allen and D.M. Coleman, *Appl. Spectrosc.* **41**, 381 (1987)

68)- R.M. Barnes and R.G. Schleicher, *Spectrochim. Acta* **30B**, 108 (1975)

69)- C.W. Fuller, R.C. Hutton and B. Preston, *Analyst* **105**, 913 (1981)

70)- R.L. Mitchell, D. Purves, R.O. Scott and R.C. Voss, *Spectrochemical Methods for the Analysis of Soils, Plants and Other Agricultural Materials*, The Macaulay Institute for Soil Research, Aberdeen (1971)

71)- N. Mohamed and R.C. Fry, *Anal. Chem.* **53**, 450 (1981)

72)- G.D. Christian, Analytical Chemistry, 4th edn., John Wiley & Sons, New York, 1986

73)- R. Jowitt and I. Abell, Comm. Eur. Communities, [Rep.] EUR, 1986, EUR 10141, 51pp.

74)- S. Sparkes and L. Ebdon, *Anal. Proc.* **23**, 410 (1986)

75)- L. Halicz and I.B. Brenner, *Spectrochim. Acta* **42B**, 207 (1987)

76)- C.S. Saba, W.E. Rhine and K.J. Eisentraut, *Anal. Chem.* **53**, 1099 (1981)

77)- R.C. Fry and M.B. Denton, *Anal. Chem.* **49**, 1413 (1977)

78)- L. Ebdon and A.R. Collier, *Spectrochim. Acta* **43B**, 355 (1988)

79)- N.J. Miller-Ihli, *J. Anal. At. Spectrosc.* **3**, 73 (1988)

80)- A. Sugimae and R. Mizoguchi, *Anal. Chem.* **144**, 205 (1982)

81)- M. Kashiki and S. Oshima, *Anal. Chim. Acta* **51**, 387 (1970)

82)- J. Stupar and R. Ajlec, *Analyst* **106**, 144 (1982)

83)- C.W. Fuller and I. Thompson, *Analyst* **102**, 141 (1977)

84)- P.T. Gilbert Jr., *Anal. Chem.* **34**, 1025 (1962)

85)- T. Ramsey, *J. Anal. At. Spectrosc.* **1**, 185 (1986)

86)- L. Ebdon, Short Course on Slurry, Winter Conference on Plasma Spectrochemistry, San Diego, 1988

87)- P.B. Farnsworth and G.M. Hieftje, *Anal. Chem.* **55**, 1417 (1983)

88)- J.L. Johnes, R.L. Dahlquist and R.E. Hoyt, *Appl. Spectrosc.* **25**, 628 (1971)

89)- R.L. Dahlquist, J.W. Knoll and R.E. Hoyt, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1975, Cleveland, Ohio, #341

90)- K. Ohls and D. Sommer, *Fresenius Z. Anal. Chem.* **296**, 241 (1979)

91)- R.K. Winge, V.A. Fassel and R.N. Kniseley, *Appl. Spectrosc.* **25**, 636 (1971)

92)- H.G.C. Human, R.H. Scott, A.R. Oakes and C.D. West, *Analyst* **101**, 265 (1976)

93)- J.Y. Marks, D.E. Fornwalt and R.E. Yungk, *Spectrochim. Acta* **38B**, 106 (1983)

94)- J. Beaty and R. Belmore, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1981, Atlantic City, New Jersey, #321

95)- C. Wohlers, R. Belmore and J. Beaty, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1981, Atlantic City, New Jersey, #322

96)- R. Belmore, R. Gordon and J. Beaty, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1981, Atlantic City, New Jersey, #323

97)- R.K. Brown, R. Belmore and J. Beaty, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1981, Atlantic City, New Jersey, #324

98)- J.S. Beaty and R.J. Belmore, *J. of Testing and Evaluation* **12**, 212 (1984)

99)- A. Aziz, J.A.C. Broekaert, K. Laqua and F. Leis, *Spectrochim. Acta* **39B**, 1091 (1984)

100)-F.N. Abercrombie, M.D. Silvester and G.S. Stoute, *ICP Inf. Newslett.* **2**, 309 (1977)

101)-J.W. Carr and G. Horlick, *Spectrochim. Acta* **37B**, 1 (1982)

102)-M. Thompson, J.E. Goulter and F. Sieper, *Analyst* **105**, 32 (1981)

103)-B.V. L'vov, *Talanta* **23**, 108 (1976)

104)-K.C. Ng and J.A. Caruso, *Appl. Spectrosc.* **39**, 719 (1985)

105)-A.M. Gunn, D.L. Millard and G.F. Kirkbright, *Analyst* **103**, 1066 (1979)

106)-G.F. Kirkbright and R.D. Snook, *Anal. Chem.* **51**, 1938 (1979)

107)-D.R. Hull, G. Horlick, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1980, Atlantic City, New Jersey, #243

108)-C.J. Park and G.E.M. Hall, *J. Anal. At. Spectrosc.* **2**, 473 (1987)

109)-C.J. Park and G.E.M. Hall, *J. Anal. At. Spectrosc.* **3**, 355 (1988)

110)-E. Kitazume, *Anal. Chem.* **55**, 802 (1983)

111)-D.L. Millard, H.C. Shan and G.F. Kirkbright, *Analyst* **103**, 502 (1978)

112)-S.E. Long, R.D. Snook and R.F. Browner, *Spectrochim. Acta* **40B**, 553 (1985)

113)-G.F. Kirkbright and R.D. Snook, *Appl. Spectrosc.* **37**, 11 (1983)

114)-R.F. Browner, *ICP Inf. Newslett.* **9**, 778 (1984)

115)-B. Strzyzewska, *Spectrochim. Acta* **26B**, 59 (1971)

116)-M. Thompson, B. Pahlavanpour, S.J. Walton and G.F. Kirkbright, *Analyst* **103**, 568 (1978)

117)-M. Thompson, B. Pahlavanpour, S.J. Walton and G.F. Kirkbright, *Analyst* **103**, 705 (1978)

118)-B. Pahlavanpour, M. Thompson and L. Thorne, *Analyst* **105**, 467 (1981)

119)-B. Pahlavanpour, M. Thompson and L. Thorne, *Analyst* **104**, 756 (1980)

120)-R.K. Skogerboe, D.L. Dick, D.A. Pavlica and F.E. Licht, *Anal. Chem.* **47**, 568 (1975)

121)-G.F. Kirkbright and R.D. Snook, *Anal. Chem.* **52**, 1983 (1979)

122)-J.M. Goldberg and K.P. Carney, *Spectrochim. Acta* **46B**, 393 (1991)

123)-J.M. Goldberg and K.P. Carney, *Spectrochim. Acta* **45B**, 1177 (1990)

124)-J.M. Goldberg and K.P. Carney, *Spectrochim. Acta* **45B**, 1167 (1990)

125)-S.Y. Suh, R.J. Collins and R.D. Sacks, Appl. Spectrosc. 35, 42 (1981)

126)-D.V. Duchane and R.D. Sacks, *Anal. Chem.* **50**, 1757 (1978)

127)-E.M.A. Clark, *Diss. Abstr. Int. B* **40**, 2153 (1979)

128)-D.V. Duchane and R.D. Sacks, *Anal. Chem.* **50**, 1752 (1978)

129)-D.V. Duchane and R.D. Sacks, *Anal. Chem.* **50**, 1765 (1978)

130)-J.S. White and A. Scheeline, *Anal. Chem.* **59**, 305 (1987)

131)-G.J. Kamla and A. Scheeline, *Anal. Chem.* **58**, 923 (1986)

132)-J.S. White and A. Scheeline, *Spectrochim. Acta* **43B**, 551 (1987)

133)-J.S. White and A. Scheeline, *Appl. Spectrosc.* **43**, 991 (1989)

134)-A. Scheeline, G.H. Lee and J.S. White, *Appl. Spectrosc.* **44**, 1183 (1990)

CHAPTER 2

There are few parameters to optimize in direct sample insertion, which is probably its chief advantage. The need to optimize the geometry of insertion probes was a recurrent theme throughout the survey of DSI presented in the introduction. The work of Lorber et al. had demonstrated the need to disperse geological materials in graphite for their direct insertion. This entailed a proportionate loss of sample, which had to be made up otherwise to keep the enviable performance characteristics reported by others.

The size of the probe that can be inserted in the plasma is limited by the need to keep a fireball lit. There must remain enough volume between the probe and the torch's walls to allow inductive coupling of energy from the load coil to the support gas. This first publication reported work done to develop a probe that could carry more sample into the plasma without further encroaching on the induction zone.

The manuscript was published as :

Probe Design for the Direct Insertion of Solid Samples in the Inductively Coupled Plasma for Analysis by Atomic Emission and Mass Spectrometry

Laurent Blain and Eric D. Salin
Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec H3A 2K6, Canada
David W. Boomer
Ontario Ministry of the Environment, Trace Contaminants Section, Toronto, Ontario M9W 5L1, Canada

JOURNAL OF ANALYTICAL ATOMIC SPECTROMETRY, DECEMBER 1989, VOL. 4, PP. 721-725

Laurent Blain carried out the experimental work, and the interpretation of the bulk of the data was done under the supervision of Prof. Salin. D.W. Boomer arranged for time on the Ontario Ministry of the Environment's ICP-MS instrument, and helped with the interpretation of the ICP-MS data.

ABSTRACT

An alternative to the conventional probes used for the direct introduction of solid samples into the inductively coupled plasma is presented. Powdered samples have been mixed with graphite and pressed into pellets, which were then inserted into the plasma. Unlike other probes, such as graphite cups, the whole body of these pellets was composed of sample mixture, so more sample could be inserted into the plasma at once. For some elements, the resulting improvements in detection limits was commensurate with the increased mass of sample whereas for other elements it was greater, suggesting that the absence of walls on the probes may result in better heat and mass transfers.

Keywords : *Direct sample introduction; inductively coupled plasma; direct analysis of solids; trace element determination*

INTRODUCTION

The Inductively Coupled Plasma (ICP) is now a well-established technique for the analysis of liquids [1]. In most applications a pneumatic nebulizer is used to convert the liquid into a finely dispersed aerosol, and a spray chamber is then used to further reduce the average droplet size of the sample mist. Only a small fraction (3-10%) [2] of the sample is eventually carried through the introduction system into the plasma, and the performance of the nebulizer is set to a great extent by the physical properties of the liquid [3]. Clearly, sample introduction is a component of ICP systems that remains in need of improvement.

Most of the samples that are routinely analyzed by ICP do not occur naturally in liquid form, and extensive sample preparation procedures are needed to convert these into a format acceptable to the existing sample insertion systems. To date, ICP spectroscopists have devised six alternative sample introduction schemes that aim to eliminate the need for extensive sample preparation :

- laser ablation [4]
- spark elutriation [5]
- electrothermal vaporization (ETV) [6]
- fluidized beds [6]
- slurry techniques [7]
- direct sample insertion (DSI) [8]

Direct sample insertion requires less complex apparatus than the first three alternatives. Although the fluidized beds are also simpler, their performance is affected markedly by variations in the physical form of the powdered samples. In particular, the transport efficiency of solid particles to the plasma will vary with their size and mass, as well as the extent to which these particles are decomposed by the plasma. Likewise, while it is an advantage of the slurry techniques that they require only minor modifications to existing sample introduction systems, their performance is limited by that of the spray chambers they use. Classes of elements are often found in matrices of differing hardness within a given sample, so that when it is ground they will be spread into different particle size distributions. If the sample and calibration standards do not break down in the same pattern, the discrimination according to particle size on which spray chambers work can lead to substantial inaccuracies [9]. Provided that all the sample is consumed in a single burn and that peak areas are integrated, direct sample insertion should be free from this type of error.

Metal powders, various salts and sample of geological origin [10] melt or sinter into globules when they are directly inserted into the ICP. For example, the direct insertion of 30 mg of pure copper powder will result in a steady signal that may last as long as 1 h as the metal on the surface of the globule is slowly boiled off. We, and other workers [10], have found that the formation of this globule is prevented by mixing the samples with graphite powder, at ratios varying from 1:3 to 1:5. Thus when copper is mixed with graphite in a proportion of 1 part to 4, a shorter, but much more intense, burst of copper emission lasting at most 5 min is observed after the direct insertion of 30 mg of this mixed sample into the ICP. Because less sample is inserted at one time into the ICP, the integrated signal is less with the mixed sample than with the undiluted copper powder, but the former time profile is much sharper. This sharper peak is more readily discriminated from the noise on its base line and thereby results in better limits of detection.

With some types of sample, the formation of a globule will result in a complete loss of signal. Brenner et al [10] have reported that when samples of geological origin formed a refractory globule no signal was recorded for all but the most volatile elements. However, when these samples were mixed with graphite powder, in a proportion of 1 part sample to 5 parts graphite, the signals of many less volatile elements were recovered. The shorter the analysis time, the better the limits of detection, and in some instances the impossibility of performing the analysis by any other method, demands that the samples be mixed with graphite powder prior to their introduction by DSI.

The basic arrangement for DSI has already been described in detail [11,12], hence this paper will restrict itself to recent improvements in the design of the probe. Although detection limits are the main concern at this stage, the reproducibility of the composition of the sample and the precision of the measurements have also been examined.

INSTRUMENTATION

The two conventional DSI probes that have already been characterized [8,13] are depicted in Figures 1-a) and 1-b). Figure 2 is a diagram of the pellet probe that is the subject of this report. The average weight of sample that can be carried by the probe of Figure 1-a) is 30 mg while the average weight of a pellet is 250 mg, which means that the latter probe could endure dilution factors of up to 1:9 and still offer the detection limits that have made DSI attractive.

Undiluted 0.0001% SPEX g-standard was first used to prepare the pellets, to allow a direct comparison of the detection limits of this DSI probe with those already reported for the graphite cup [8]. Then, when the need for calibration standards of lower concentration arose, a suitable amount of sample was mixed with enough graphite powder to make up a total mass of 1.250 g from which five replicate pellets could be produced. The powder was then manually briquetted with a pellet press of the kind used in calorimetry, using a custom made hardened steel punch and die set of 3/16" diameter. The particulars of materials, tools and instruments that were used for this work are listed in Table 1.

A Thermo Jarrell Ash ICAP 61 direct reading spectrometer was used to acquire all the ICP-AES data that will be presented in this report. The control of the instrument is distributed between two processors, an on-board controller and an IBM AT compatible microcomputer which communicate via a serial link. The software provided with the instrument, ThermoSpec, proved too restrictive for our application, so a custom program was written in Pascal to take greater advantage of the controller's options.

The exposure sequence used was a variation on the standard SPECTRUM SHIFT option [14], in which a refractor plate immediately behind the entrance slit is used to move the image at the exit slit.

The mass spectrometry (MS) data was obtained on a SCIEX ELAN 250, equipped with a direct sample insertion system that has been described elsewhere [15]. The settings of the mass spectrometer are listed in Table 2, along with the inductively coupled plasma's operating conditions and the direct insertion devices parameters for both the AES and MS measurements.

RESULTS AND DISCUSSION

The rationale behind the use of a pellet as a DSI probe was that it would result in lower detection limits by increasing the mass of sample introduced in the plasma per unit time. Two features of the pellet are advantageous in that respect, the first obvious is its larger mass which should result in a proportional increase of the integrated signal if all the sample is consumed. The other is the absence of solid walls around the sample, which should result in a better transfer of heat from the plasma to the sample as well as a better mass transfer of analyte from the probe to the plasma, and thus give narrower, more intense peaks.

These first investigations were primarily concerned with establishing that the larger mass of sample inserted in the plasma was entirely consumed, and did indeed lead to a commensurate increase in signal. Other workers [8] have already established the detection limits for undiluted SPEX g-standards with graphite cups, and this material was also used in these experiments. The detection limits of two elements, Pb and Sn, are compared for the pellet and graphite cup probes in Table 3. The improvement in detection limits is of about a factor of eight for Sn, as would be expected from mass considerations alone; the improvement is somewhat greater for Pb, which suggests that the other effects mentioned above may be significant.

The detection limits of Table 3 were calculated as the ratio of three times the standard deviation of the off-line background to the peak intensity of the signal for pellets made from 1 μg/g SPEX g-standard. The variance of the on-line and off-line signals for graphite blanks were compared by an F test and were found not to differ significantly at the 95 % confidence level. Provided that at least one of the two off-line positions of a given channel is not corrupted by a spectral interference, it is legitimate to use the variance at that position as an indicator of the blank noise in the formula for detection limits. A spectral interference at one of the off-line positions could easily be visually determined, or a more sophisticated algorithm could be used to perform this check automatically in the data processing program.

With transient signals, the use of peak areas results in better precision than peak height. However, it may be easier to extract peak height from weak signals on a noisy background, which in turn could result in better detection limits. To see whether peak height could be used to advantage in this technique, another set of detection limits was calculated as the ratio of two times the noise of the off-line background to the peak intensity of the signals. Both sets of detection limits are compared in Table 4 and clearly the use of integrated signals is also advantageous in terms of sensitivity.

These initial limits of detection fell well below the least concentrated SPEX g-standard, by about two orders of magnitude on average, and more dilute standards had to be prepared to calibrate the technique in its lower concentration range. The principal difficulty in the dilution of solid standards lies in the mixing operation, which can lead to substantial heterogeneity in the composition of the mixed standards [16,17].

A mixing procedure may be considered adequate if it does not significantly enhance the pellet to pellet variance on peak area for the mixed standards, compared with that of the starting material. With the g-standards it was found that the variance on peak area with pellets is about 7%, and this is also what others have reported for the same standards with graphite cups [8].

The 10 μg/g SPEX g-standard was first mixed with graphite powder in a ratio of 1 to 9, using a mechanical mixer/mill. Five pellets were pressed from each batch and the pellet to pellet reproducibility was compared with that of undiluted 1 μg/g SPEX g-standard as a check on the mixing operation. The typical pellet to pellet variance on peak area was about 70% to 200%, yet the average peak areas were not significantly different from batch to batch.

Visual examination of the mixing chamber indicated that after a few seconds of operation the single mixing bead had established a constant path through the powder. Furthermore, when the chamber was opened and the powder was gently tapped out it came in two separately identifiable lots. The first portion was very much like the original powder and came off the walls where the bead had not struck, then the powder that had been in the path of the bead could be scraped off the walls of the chamber and came out in cakes. Evidently, the powder in the bead's path was being efficiently crushed, but the two parts of the composite standards were not being adequately blended in this operation. What seemed to be required was a randomization of the motion of the bead through the powders.

Other mixing procedures were tried, and it was found that the best results were obtained with a mixing chamber of 60 cc with 10 mixing beads and manual agitation. Using this procedure, the variances of peak areas and peak heights for mixed standards were about the same as those usually obtained with undiluted SPEX g-standards in our laboratory. Linear calibration graphs were thus established in the 0.75-10 μg/g range with an average standard error on the slopes of 10%. Some typical errors on the slopes of these calibration graphs are listed in Table 5.

Molybdenum may form a refractory carbide with the surrounding graphite matrix, which often results in a complete suppression of the signal for that element. This explains the anomalously high error of its calibration curve's slope in Table 5. This type of chemical interference presents a serious problem only for the determination of elements in Groups IVa-VIa of the Periodic Table, which form stable high-melting metallic carbides and of the rare earth elements and actinides, which form stable heteropolar carbides [18,19]. Furthermore, in many instances the formation of refractory carbides has been successfully circumvented by the use of volatilization enhancers such as NaF [8] and a series of chlorides [20].

The limited range of concentrations that is covered by the calibration curves of the data of Table 5 does not correspond to the linear dynamic range of the technique, but is due to an instrumental limitation which we are currently overcoming. Our direct reader's controller was designed for steady state signals, and it does not deal well with transient signals. The only option that allows consecutive time resolved off-line and on-line exposures to be recorded is the SPECTRUM SHIFT option, in which a single integration time must be used for all the channels. Because the total number of exposures is fixed at 64, a compromise must be reached between the short integration times that are necessary to adequately resolve the short signals from shifts in the plasma's background emission, and the longer integration times needed to completely record the slower signals. Typically, either the fast signals of Cd, Hg and Pb appear as a single point in the timescans, or the long signals of Fe, Mn and Ni are prematurely cut off. This dilemma is depicted in Figures 3-a) and -b). Recent experiments with a spectrometer identical to the ICAP 61 in all respects but that the controller has been replaced by an IBM PC based system marketed by Technical Service Laboratories [21] have demonstrated that the limitations are in no way inherent to the hardware itself. Rather, it is the controller's program that does not fully exploit the possibilities latent in the instrument's design, so that the solution lies in a simple upgrade of the software of the system.

Whether the off-line background signal is a valid estimate of the analytical blank for these determinations depends on the level of contamination of the graphite diluent by the elements of interest. Most elements were not present at detectable levels in the graphite powder that was used in these experiments, hence a procedure could be developed for the blankless, calibration curve based, determination of those elements. However, five elements (Cr, Cu, Fe, Ni and Zn) were present at levels high enough in the graphite powder to give rise to significant signals, so that blank measurements would be required for the determination of these elements, unless a prior purification of the graphite powder was carried out.

Reference sediment materials BCSS-1, MESS-1 and PACS-1, are supplied by the National Research Council of Canada (NRCC). These sediments have been dried and ground, and represent the type of materials we have targeted. In all instances, the concentration of the elements in the sediments was at least an order of magnitude above the detection limit of the method, even after a tenfold dilution of the samples.

Although the detection limits obtained with a pellet are low enough to make the analysis of these materials possible with this technique, lower detection limits would still be an asset. The concentration reported for these materials are average concentrations taken over the whole bulk. The local composition of a small sample may be very different to the average concentrations, due to either the poor homogeneity of the material or to the segregation of some elements. It is thus possible that the effective concentration of some elements in these samples will be dangerously close to the limit of detection of the technique, thereby limiting its utility in the study of the composition of that material.

For example, the standard reference materials have undergone extensive pre-treatment, and still the supplier recommends that a minimum weight of 500 mg be used to ensure that the error on the determination be less than 5% at the 95% confidence level. As there is a limit to how large a sample can be inserted into the plasma, it is possible that some pellets will have concentrations that fall below the detection limits for some of the trace elements. In this instance, the lower detection limits afforded by ICP-MS would enhance the usefulness of DSI both for the determination of unbiased average concentrations and for the study of the distribution of analytes in the bulk of the material.

Inductively coupled plasma MS offers an appreciable gain in sensitivity over ICP-AES [22] but, because it involves physical sampling of the ICP, it is more prone to contamination by concomitants in complex matrices. The sampling orifice of the mass spectrometer can get progressively clogged by residues from the sample, and any undissociated species that make it past the sampler can eventually degrade the performance of the mass detector. The suitability of the pellet DSID as a sample delivery system for the ICP-MS was evaluated over the course of one week. During this time, the performance of the instrument did not degrade noticeably. Samples prepared from the SPEX g-standards and graphite were used throughout these experiments, and in the course of five consecutive days no discernible deposit of carbon occurred on the sampling orifice. In general, the reproducibility of the signals was less than 15 %, which is an acceptable range for mixed solid standards.

The current version of the ELAN was not designed to simultaneously record many transient signals, so only one mass channel was used throughout these MS investigations, Pb 207. Lead is of considerable importance to environmental scientists and is usually found at very low levels in materials of natural origin, hence our interest in this element. The detection limits for lead by three DSI arrangements are compared in Table 6; ICP-MS provides an improvement of about three orders of magnitude over ICP-AES.

CONCLUSION

The increased mass of sample that can be inserted in the plasma has resulted in significant improvements in detection limits. This allows dilution factors of up to 1:9 to be used without losing the attractive detection limits that this technique offers. Furthermore, the larger masses of sample that this probe can handle are not only easier to handle, but they may offer an advantage in terms of sampling statistics. Because the range of masses that can be used is roughly an order of magnitude greater with the pellets than with the conventional graphite cup probes, it will now be possible to quantitatively express the degree of homogeneity of the bulk material [17]. With this information, it will be possible to tune the preparation procedure for the type of bulk material, the particle size, the minimum dilution ratio, and the number of increments needed to get a representative sample.

The authors wish to thank A. Kluck and B. Bastian of the machine shop of the Department of Chemistry, McGill University, for their assistance in the design and construction of the pellet DSID.
The majority of this work was funded by a grant from the Ontario Ministry of the Environment, Project 270RR.
L. Blain acknowledges the financial support of the Natural Sciences and Engineering Research Council of Canada.

Table 1

Powders :	
SPEX g-standards	spex industries, inc. Metuchen, New Jersey
briquetting graphite powder	spectroscopic electrodes bay carbon, inc. Bay City, Michigan
Mechanical mixer :	
5100 spex mixer/mill	spex industries, inc. Metuchen, New Jersey
Press :	
pellet press	parr instruments company Moline, Illinois
Microcomputer and software :	
ibm-at compatible pc	ast premium 286 AST RESEARCH, INC. Irvine, California, U.S.A.
Pascal compiler	turbo pascal BORLAND INTERNATIONAL Inc.
Scotts Valley, California, U.S.A.	
Spectrometers :	
Direct reader	TJA ICAP 61 Thermo Jarrell Ash Corporation Franklin, Ma, U.S.A.
ICP-MS	Perkin Elmer sciex elan 250 Perkin-Elmer Co. Norwalk, Ct,U.S.A.

Table 2

ICP-AES

- ICP parameters :
  - Forward power : 1.5 KW
  - Reflected power : 0-80 W
  - Tuning : automatic
  - Flow rates :
    - Plasma : 16 L/min
    - Auxilliary : 2 L/min
- Spectrometer parameters :
  - Viewing height : 15 mm
  - Integration time : 1.5 s up to 1 μg/g
    - 5.0 s up to 10 μg/g
  - 2 off-line spectrum shifter positions
  - average wavelength offset : 0.15nm
- DSI parameters :
  - Pre-heat height : -20 mm(1)
  - Pre-heat : 10 s
  - Insertion depth : - 2 mm(1)
  - Insertion : 120 s up to 1 μg/g
    - 350 s up to 10 μg/g

ICP-MS

- ICP parameters :
  - Forward power : 1.0 KW
  - Reflected power : 0-80 W
  - Tuning : automatic
  - Flow rates :
    - Plasma : 16 L/min
    - Auxilliary : 2 L/min
- MS parameters :
  - Mass channel : 208 a.m.u.
  - B ion lens setting : 50
  - P ion lens setting : 50
  - Dwell time : 20 ms
  - Points per scan : 3
  - Scans per run : 605
- DSI parameters :
  - Pre-heat height : -20 mm(1)
  - Pre-heat : 10 s
  - Insertion depth : - 4 mm(1)
  - Insertion : 40 s

(1) - All DSI heights are measured as the distance from the top of the ICP load coil to the top of pellet

Table 3

Detection limits in undiluted SPEX g-standards by DSI-ICP-AES, using a graphite cup and a pellet.

	Detection limits, ng/g	
Element	Graphite cup(1)	Pellet(2)
Pb	330	24
Sn	60	8

(1) - 30 mg average sample load [8]
(2) - average weight of pellet : 250 mg

Table 4

Detection limits for seven elements in undiluted SPEX g-standards by pellet DSI

	Detection limits, ng/g	
Element	Integrated signal	Peak height
Cd	13	20
Fe	1	13
Hg	10	14
Mg	1	5
Mo	760	1000
Pb	24	40
Sn	8	13

Table 5

Typical errors on the slopes of calibration graphs with pellet DSI(1)

Element	Standard error on slope (%)
Cd	9
Fe	15
Hg	3
Mg	8
Mo(2)	54
Pb	8
Sn	21

(1) - Concentrations ranged from 750 ng/g to 10 µg/g

(2) - Mo has anomalously high error on slope because it forms carbides with graphite matrix, see text for explanations.

Table 6

Detection limits for lead with three DSI systems

ICP-AES	- graphite cup	965 ng/g
	- pellet(1)	118 ng/g
ICP-MS	- pellet(2)	0.02 ng/g

(1) - corrected for 1:9 dilution g-standard/graphite

(2) - corrected for 1:19 dilution g-standard/graphite

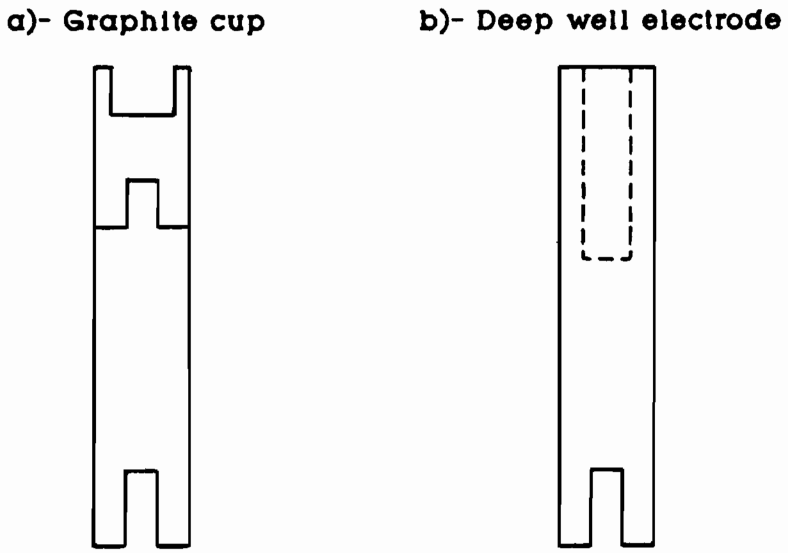


Figure 1

Two conventional probes for the direct insertion of solids into the ICP. A, Graphite cup and B, deep well electrode

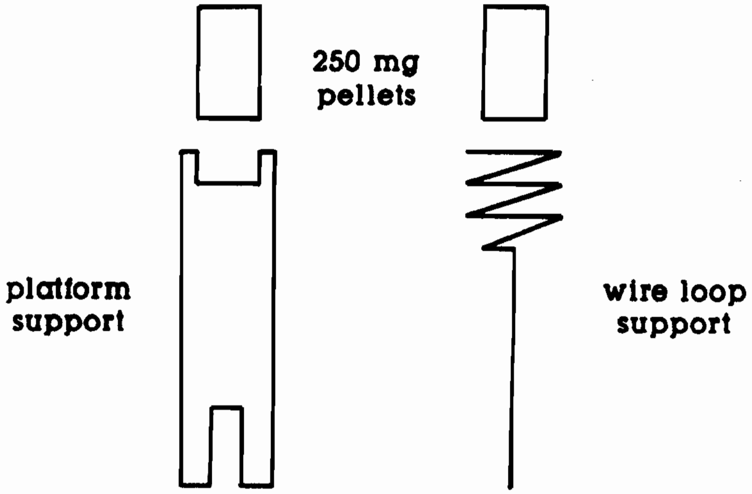


Figure 2

Two arrangements for the pellet direct sample insertion device

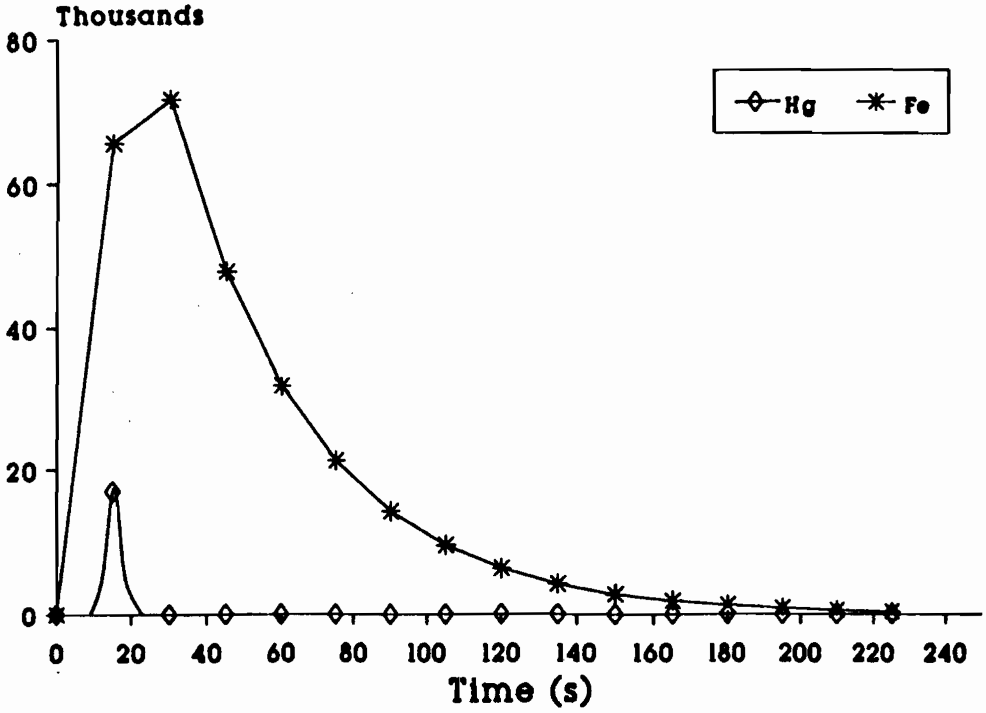


Figure 3.a)-
Net emission signal of Fe and Hg with integration time set for Fe (see text for explanation)

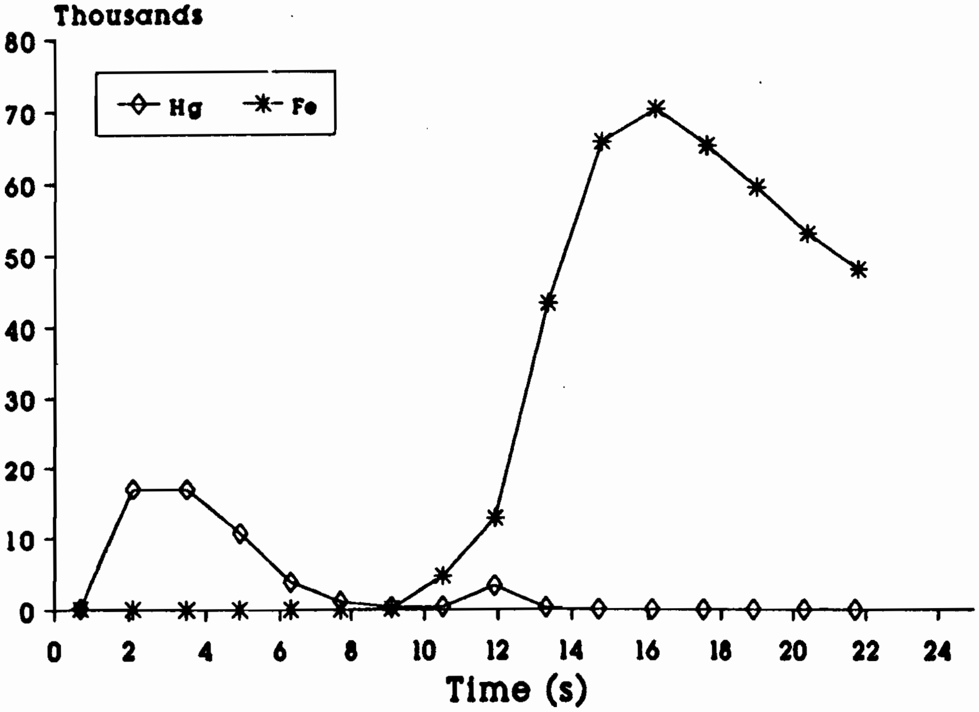


Figure 3.b)-
Net emission signal of Fe and Hg with integration time set for Hg (see text for explanation)

REFERENCES

1 - G.A. Meyer, *Anal. Chem.* **59**, 1345A (1987)

2 - B.L. Sharp, *J. Anal. At. Spectrom.* **3**, 939 (1988)

3 - B.L. Sharp, *J. Anal. At. Spectrom.* **3**, 613 (1988)

4 - M. Thompson, J.E. Goulter and F. Sieper, *Analyst* **33**, 106 (1981)

5 - R.H. Scott, *Spectrochim. Acta* **33B**, 124 (1978)

6 - P.W.J.M. Boumans, Ed.; *Inductively Coupled Plasma Emission Spectroscopy - Part 2 Applications and Fundamentals*; Chemical Analysis series vol. 90, John Wiley & Sons, Inc: New York, 1987

7 - L. Ebdon and M.R. Cave, *Analyst* **107**, 172 (1982)

8 - Y. Shao and G. Horlick, *Applied Spectrosc.* **40**, 386 (1986)

9 - J.F. Tyson, S.A. Darke, S.E. Long, and C.J. Pickford, paper B26, Fifteenth Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Boston, Massachusetts, 1988.

10 - I.B. Brenner, A. Lorber and Z. Goldbart, *Spectrochim. Acta* **42B**, 219 (1987)

11 - R.L.A. Sing, Ph.D. dissertation, McGill University, 1986

12 - R.L.A. Sing and E.D. Salin, *Anal. Chem.* **61**, 163 (1988)

13 - C.J. Monasterios, A.M. Jones and E.D. Salin, *Anal. Chem.* **58**, 780 (1986)

14 - T. Toothaker, documents no. EN-1186 and EN-1187, Thermo Jarrell-Ash Corporation

15 - D.W. Boomer, M.J. Powell, R.L.A. Sing and E.D. Salin, *Anal. Chem.* **58**, 975 (1986)

16 - C.O. Ingamells, *Talanta* **21**, 141 (1974)

17 - B. Kratochvil and J.K. Taylor, *Anal. Chem.* **53**, 924A (1981)

18 - H. Nickel, *Spectrochim. Acta* **23B**, 323 (1968)

19 - J. Bril, *Spectrochim. Acta* **23B**, 375 (1968)

20 - H. Nickel, M. Reisch and M. Mazurkiewicz, paper F5.1, XXV Colloquium Spectroscopicum Internationale, Toronto, Canada, June 21-26, 1987

21 - G. Légère and P. Burgener, *ICP Inf. Newsl.* **13**, 521 (1987)

22 - G. Horlick, S.H. Tan, M.A. Vaughan, and Y. Shao, Inductively Coupled Plasma - Mass Spectrometry; **in** Montaser, A.; Golightly, D.W., **Eds.**; *Inductively Coupled Plasmas in Atomic Spectrometry*; VCH Publishers Inc: New York, 1987.

CHAPTER 3

The potential of DSI for the analysis of solids has been established by many workers. However, a controversy remains as to whether the technique can handle the more complicated matrices of geological materials. The impact of the insertion of a probe on the plasma's performance characteristics has only recently been systematically documented. The materials studied so far have all been virtually thermochemically inert : graphite, coals, ceramics and Ni based alloys. It has already been shown how the direct insertion of undiluted geological samples resulted in erratic burns and poor signals unless the sample was dispersed in graphite by factors of as much as 1:5.

The sole report that attempted the direct insertion of geological samples was not truly representative of DSI, because it used lateral rather than axial insertion. Axial insertion minimizes the disturbance of the plasma's fireball and its outer gas flows, often a central channel is formed as in conventional systems. Reports on the performance characteristics of DSI have established that the speed and depth of axial insertion are critical factors. Lateral insertion disrupts the flow pattern of plasma gases and the position of the probe in the discharge cannot be optimized.

The direct insertion of pellets prepared from mixtures of sediment and graphite was attempted and the results have been accepted for publications as :

Observations on the Use of Pellet Direct Sample Insertion for Inductively Coupled Plasma Atomic Emission Spectrometry

Laurent Blain and Eric D. Salin
Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal,
Quebec H3A 2K6, Canada
SPECTROCHIMICA ACTA, PART B - TO BE PUBLISHED

Laurent Blain carried out the experimental work and the interpretation of the data, under the supervision of Prof. Salin.

ABSTRACT

The feasibility of analyzing geological materials by the use of the direct sample insertion (DSI) technique into the inductively coupled plasma was assessed with a sediment reference material, PACS-1 (NRCC). Sharp and intense peaks were recorded for elements of high and intermediate volatility (As,Cd,Cu,Hg,Mn,Pb,Se,Sn,Zn) after the insertion of pellets prepared from 1:5 mixtures of PACS-1 in graphite.

Probe geometry and plasma RF power were optimized to enhance both the magnitude of the signals and the temporal resolution of spectral overlaps. A variable integration time base was found essential to allow good observation of the signals of analytes ranging from volatile trace level elements to refractory matrix constituents.

The use of thermochemical additives to enhance the vaporization of refractory elements was investigated. It was found that chloride releasing reagents were preferable to fluoride salts, because the fluorides caused a sudden massive release of Si into the plasma, which resulted in severe physical and spectral interferences.

INTRODUCTION

Since the first reports by Salin and Horlick [1] and Sommers and Ohls [2], the direct insertion of samples into the inductively coupled plasma has shown great promise for the determination of trace and ultra trace elements. A recent publication by Karanassios and Horlick [3] reviews the development of direct sample insertion (DSI) in terms of instrumentation and methodology. It also provides an exhaustive survey of the types of materials that have been analyzed by DSI and the performance characteristics that were reported by the various groups working on this technique.

With few exceptions, the reports that have been published so far on solid analyses by DSI concentrated on establishing performance characteristics [4-7], and their scope was limited to simple materials on the whole. McCleod et al. [4] determined volatile elements in Ni base alloys, Pettit and Horlick [5] determined volatile elements in coals and botanicals, Shao and Horlick [6] did the same in powdered arc standards (i.e. SPEX g-standards), and Broekaert et al. [7] in aluminium oxide. In every case, it was found that volatile elements could be determined at levels down to a few parts per billion (ng/g), and that matrix effects were not a problem. The refractory elements were found to leave the probe better when volatilization enhancers were used [6,7]. These thermochemical additives are chloride or fluoride releasing salts, such as AgCl and NaF, that combine with these elements to form volatile compounds.

In stark contrast, the appraisal of Brenner et al. [8] is very pessimistic based on their work with synthetic silicate standards and various geological samples. They concluded that matrix interferences are abundant during volatilization, with dire consequences for the technique's calibration. The main thrust of their argument is that the analyte's volatilization is not determined by the same thermal properties in synthetic standards as in naturally occurring geological materials. This, they argue, is because the elements in a synthetic standard are present as salts, while they are bound in naturally occurring silicate minerals.

It is difficult to reconcile this last report's dismissal of DSI with the other reports. Strictly speaking, approach of Brenner et al. is not representative of DSI because it uses horizontal insertion into the "tail flame" of the plasma discharge [8] as opposed to all other DSI work being based on axial insertion systems [3]. A close examination of the various reports published on the optimization of DSI systems [3] would lead to the *a priori* prediction of inferior performance for the horizontal insertion systems. Nonetheless, the work of Brenner et al. indicates that geological materials present a more difficult matrix and provide a worthwhile challenge. A logical approach requires that the various classes of matrix interferences be investigated individually, as much as possible. These range from sampling effects, depending on the homogeneity of the analyte's distribution in the sample, to physical interferences resulting from the insertion of the probe and the sudden release of elemental vapors into the plasma. They may even include chemical interferences either in the probe or the plasma.

This and a companion paper [9] will report work that has been done in our laboratory toward the development of instrumentation and procedures appropriate for the analysis of geological sediments by DSI. We feel that sediments represent a good "test case" for the application of DSI to the analysis of geological materials, in terms of sampling and of bulk chemical composition. The first of these reports describes the development of a procedure that allows the direct insertion of sediments in the plasma and the acquisition of reproducible signals. The methodology of DSI analyses is discussed in the next paper, with a particular emphasis on the technique's calibration.

EXPERIMENTAL

Direct Sample Insertion

There are many variations on the theme of computer controlled direct sample insertion devices (DSID) [3]. The vertical stepper motor driven system designed by Sing and Salin [10] was used for this work. The principal advantage of this system is that it is entirely controlled by a microprocessor subordinate to the data acquisition system. Technical details on the components of the system are given in Table 1, the CENTROID BIG STEPPER controller comes equipped with an on-board BASIC programming language and can be interfaced to another processor via an RS-232 serial communication port. This ancillary processor keeps the operation of the DSID hidden from the data acquisition system, and their synchronization is ensured by a strict communication protocol.

A typical DSI insertion sequence is illustrated in Figure 1. It consists of six steps which may be linked to form a continuous smooth motion, or may be separated by various delays. For example, the preheat step may have a duration of a few seconds or may be dispensed with, in which case the insertion would appear as a single step. The principal advantage of a stepper motor driven system is that all the insertion's parameters are set in software [10], as opposed to a pneumatic system which relies on solenoid triggered stoppers [11] for positioning. This is a definite advantage for the development of insertion procedures and greatly simplifies the optimization of the DSID parameters.

The stepper motor controller can monitor the status of up to eight input switches. One is used as a permanent reference, e.g. with the DSID's shaft fully retracted. The status of that switch can also be monitored to retract or shut a solenoid activated flow stopper at the base of the plasma torch. This, in turn, allows the continuous operation of the plasma, in contrast to earlier systems where the plasma was extinguished between runs [12,13].

Probes

The sample carrying probes form an integral part of the DSI method. They can be graphite cups, which are essentially the same as the electrodes used with d.c. arcs [1], metal boats [5] or wire loops [10]. In a recent report [14] we introduced a probe for DSI in which the sample is pelletized in a graphite binder and held in a wire basket.

In this work three different types of DSI probes were used as indicated in Figure 2. The first, Figure 2-a, is a conventional d.c. arc type electrode. The second probe, Figure 2-b, consists of a graphite/sample pellet held within a wire basket. The evolution of this design has been discussed extensively [14] and aspects will be mentioned again below. The third probe type, a customized cup based system in which a pelletized sample has been placed is illustrated in Figure 2-c. The geometry of these cups was optimized as we will discuss.

Sediment cannot be directly pelletized with small laboratory presses, so it must first be mixed with briquetting graphite. Briefly, sediment and graphite are mixed in a ratio of 1:5 following a procedure described previously [14], and a small laboratory press of the type used in calorimetry is used to form the pellets. More details on the press, punch and die sets, briquetting graphite, and the sediment reference materials can be found in Table 2.

A major concern in the quantitative determination of trace concentrations of common elements in poorly characterized materials is contamination by reagents, and this is one of the prime arguments for the direct analysis of solids [15]. It was found that the nature and extent of the contamination of BAY CARBON's pelletizing graphite by heavy metals remained consistent from batch to batch. Contamination by Si was the worst, followed by Fe, Mn, Cu and Zn, in order of importance. Contamination by the refractory elements was investigated when thermochemical additives were studied. It was found that Al, Cr and Ni were the only other elements present in the graphite powder at levels detectable by this technique. In the assays supplied with 99.999% grade reagents by the manufacturer (Aldrich Chemical Co.), none of these elements were reported as contaminants in the four salts used (NaF, AgCl, $BaCl_2$ and NH_4CL). Furthermore, their systematic presence with all four volatilization enhancers and the comparable intensity of their signals from one to the other were strong evidence that these elements are present in the graphite powder and are not a result of a contamination by the salts.

Fe and Mn are the major constituents of steel and their most likely source is abrasion of the punch and die set used to press the pellets. It was found that when new punch and die sets were conditioned with twenty blank pressings, contamination by these two elements was reduced below detectable levels. To keep the conditioning procedure simple, five blank pellets were pressed at a time and only the last inserted. Usually, the level of contamination dropped sharply between the tenth and fifteenth pellets. Once conditioned, the punch and dies sets were used for more than 500 pressings with minor Fe and Mn blank interferences only.

Cross-contamination is another nagging difficulty with powders, because the sample preparation equipment cannot be conveniently rinsed. A simple cleaning procedure was devised whereby the punch and die are cleaned with a round brush with stiff bristles, such as those used to clean burettes, followed by five blank pressings. Once more, the fifth pellet is inserted to verify the absence of cross-contamination. This procedure was found to work well until the punch and die sets had been used long enough that the surface of the die had become scarred. This usually became a problem after pressing between 400 and 600 pellets.

Then, it took more than 25 pressings to get rid of the Si carry over from mixtures of sediment to blanks of pure graphite.

The dilution ratio of sediment in graphite was optimized for the various probe geometries, as a compromise between minimizing physical and chemical interferences and keeping low detection limits. A higher ratio of graphite to sample results in smoother burns, but the decreased sample mass results in commensurate sensitivity losses [14]. With the graphite cups, it was found that smaller pellets held in cups with thicker walls heat more slowly and the burn proceeds more smoothly. Furthermore, deeper wells contain the escaping analyte vapors more tightly in a central channel through the plasma, which greatly improves its performance. Thus, the reduced mass of the pellets that can be held in graphite cups is more than offset by the increased proportion of sediment to graphite that these pellets can contain.

Spectrometer

Commercial direct readers are meant to record steady state signals, and this is reflected in their controller's design. Previous experience with a Thermo Jarrell Ash ICAP 61 had shown that the instrument's spectrum shifter and electronics could handle the transient signals of DSI for solids [14]. The instrument's controller set the limit to its usefulness for DSI, mainly because of its limited memory capacity. Burgener and Légère [17] of Technical Service Laboratories had reported upgrades to a Jarrell-Ash Atomcomp 90750 ICAP spectrometer that showed promise of being a suitable detector for DSI, and it was used for all the work reported here.

The upgrade consists of two major changes to the commercial instrument's hardware. The spectrometer's controller is replaced with an IBM PC compatible microcomputer, and the original channel cards are replaced with faster electronics that support integration times shorter by about an order of magnitude. By replacing the system's controller with an IBM PC, it was possible to rewrite the data acquisition procedures. Custom exposures could then be implemented, provided that they adhered to the standard data acquisition sequence imposed by the channel cards [17,18].

RESULTS AND DISCUSSION

Undiluted Sediment with a Graphite Cup

Undiluted PACS-1 was first inserted directly with a conventional graphite cup (Figure 2- a) resulting in very erratic burns. The insertion of the cup was followed immediately by a bright burst of orange (Si) followed by a sequence of pink (Ca), purple, blue and green (C) emissions. Occasionally, incandescent particles were ejected from the cup and shot across the plasma like fireworks, and soot deposits collected in the corners of the plasma box after a few burns. A few seconds after the probe's insertion, the burn died down considerably and only a very dim central channel of orange emission remained.

During the burn's first few seconds, the plasma was visibly and audibly disturbed and appeared to oscillate within the confines of its induction coil. Erratic baselines were recorded at every channel monitored. The unstable plasma background emission was compounded by stray light interferences, arising from the many bright bursts of visible emission. The analyte signals seen during this period were also very poor. Split peaks were occasionally seen but were difficult to discriminate from baseline fluctuations.

It was difficult to confirm the presence of many analyte signals, because both signals and baselines changed dramatically from insertion to insertion. The signals of Fe and Mg, which are both major matrix constituents (Table 3) with intense ICP emission lines, could only be resolved from their baselines around their peak's maximum. The signals of trace elements, Cd, Hg and Pb for example, were much weaker and consequently were difficult to discriminate from baseline features.

During the later period of the insertion, the plasma settled back down to its normal state. With the exception of the Si channel, the on-line signals became noticeably steadier at this point, and the spectral background was featureless at most channels. Brenner et al.[8] reported the complete loss of signals approximately ten seconds after the direct insertion of undiluted geological materials in the plasma and attributed it to the formation of a refractory glassy globule. We confirmed this with our own work. A series of interrupted burns left a refractory globule about ten seconds after the insertion of undiluted PACS-1. When graphite cups were pulled out of the plasma less than six seconds after their insertion, they were found to still contain loose powder. On the other hand, those that were pulled out more than twelve seconds after insertion contained a shiny solid bead. The cups that were pulled out during the transition period, from six to twelve seconds, contained mixtures of loose powder and small irregular beads enmeshed in a network of brittle strands.

Insertion of Pellets of Sediment Held in Wire Baskets

The rationale behind using pellets instead of graphite cups was to increase the mass of sample inserted in the plasma and to improve the contact between sample and plasma. It was found that increased mass resulted in a commensurate improvement of detection limits [14] and sampling statistics. With 30 mg of pure g-standards, a typical load for graphite cups, the RSD on peak area deteriorated at concentrations below 1 μg/g for most elements. In absolute terms, this corresponds to a threshold mass of analyte of 30 ng. On the other hand, the typical weight for a pellet was 250 mg, an eight fold increase in sample mass which should have resulted in noticeably improved precision at that concentration and pushed the threshold concentration lower. Indeed, the RSD on the average peak area at 1 μg/g was back down to its normal DSI level (ca. 7%) [6,14]. At concentrations less than 0.09 μg/g, which corresponds to roughly the same absolute mass of analyte, the RSD again started to deteriorate.

A standard procedure for the analysis of geological materials by d.c. arc emission spectroscopy is to disperse the finely ground samples in graphite. This prevents the formation of glassy globules in the electrode's sample cavity and results in a sharp increase of volatilization rates [19]. Likewise, Brenner et al. [8] found that diluting geological samples with graphite powder not only prevented the formation of glassy globules, but also considerably smoothed out the burns. This, in turn, resulted in cleaner baselines and sharper peaks.

The performance characteristics of DSI have been established using simple materials that were themselves practically inert [4-7], allowing a full load of sample to be used. Dispersing sediments in graphite limits the amount of analyte that can be inserted into the plasma to a fraction of the graphite cup's capacity. This, in turn, entails a deterioration of the technique's detection limits. This concern motivated our work done on the development of DSI probes based on pellets instead of graphite cups [14]. As expected, this work reported detection limit improvements proportional to sample mass.

Our studies with pellets for this work began with mixtures of sediment in graphite in varying proportions. These were pressed into pellets, and inserted into the plasma held in tungsten wire baskets [14]. Soon after their insertion, these pellets shattered and extinguished the plasma. Visual observation of the plasma suggested that large volumes of gas were pushing the discharge out of its induction coil. For a brief moment immediately after the probe's insertion, the plasma oscillated axially in the coil, occasionally almost dying out and reigniting, but once the pellets heated up and shattered the plasma was systematically extinguished. To no avail, the ratio of sediment to graphite was diminished until it accounted for less than 10% of the probe's mass. A much milder, but similar problem had been encountered in previous work with pellets [14]. It had been solved by baking the pellets in an oven set at 130°C for a two hours. Even a pre-heat of up to 24 hours at temperatures as high as 250°C did not permit the uninterrupted direct insertion of sediment pellets when they were held in wire baskets. Geological samples do not readily release water molecules and OH in clay minerals at this temperature, and usually roasting is required. Furthermore, liquid and gas inclusions may often not burst at low temperatures. On the other hand, the higher temperatures called for have the attendant risk of volatility losses for low boiling elements like As and Hg.

Our previous experience with in-situ drying of liquid samples on wire loops [11] under the base of the plasma suggested that the plasma's heat could be used advantageously to carry out a thermal pre-treatment of the samples immediately prior to their insertion. The pellets were brought close to the plasma's base. Immediately the appearance of the plasma changed; it constricted and grew brighter. This is expected since the in-situ desolvation of liquid samples has the same effect on the plasma [11]. Clearly, the plasma's heat affected the sediment's matrix causing the release of gases. Indeed, when the pellets were brought very close to the base of the plasma during the pre-heat step, the plasma oscillated and was often deformed by gases escaping from cracks in the pellets. The pellets could only be inserted into the plasma once it had settled back to its original position and appearance, and a faint orange glow appeared under its base where it was closest to the pellet. This orange glow was used to gauge the pre-heat step's duration and was reproducible to within a few tenths of seconds for a given dilution ratio.

During the first few seconds of the pre-heat step, as the plasma grew brighter, the background intensity rose sharply at all channels. The channels of the trace elements had been configured for maximum sensitivity and often saturated during this period. As the pre-heat proceeded, the background fell gradually, and it became possible to discern a signal at the channels of the very volatile elements. Instead of the sharp peaks observed for these elements with metal oxide standards [6,14], these signals were weak swells not easily distinguished from their surrounding background. Figure 3 shows the background corrected signals that were recorded at the As, Cd, Hg, Pb and Zn channels during this period.

The plasma is pushed up by the pellet as it is inserted, and the insertion must be rapid and deep to successfully penetrate the plasma. Otherwise, the plasma rides on top of the pellet and is often pushed out of the induction coil. Immediately after insertion, the plasma was entirely infused by very bright orange emission, and the bright white hot core virtually disappeared as the whole plasma glowed orange. During this period, which lasted about three minutes, the plasma was visibly disturbed and audibly noisier. Even at low proportions of sediment in graphite, which resulted in smoother burns, there frequently were bursts of material released into the plasma's body as the pellets cracked. This pushed the plasma up and down in the load coil and gave surges of orange emission.

At a ratio of 1:8 PACS-1/graphite, the orange emission goes through an obvious peak after about twelve seconds and starts a slow smooth decay that lasts about two minutes. The on-line signal of silicon saturated the integrating capacitor of that channel's electronics; however, silicon's signal could be recorded by moving the alignment of the channel onto the line's shoulder with the spectrum shifter [17]. That signal's time profile is shown in Figure 4. When the orange emission had died out, the base of the plasma started to glow bright green for three to five seconds, then the whole plasma glowed blue, purple and finally pink in quick succession. The pink period lasted more than five minutes, but its full duration was never determined because the probe had been inserted in the plasma for almost ten minutes by then, and the wire loop support was beginning to deform. Previous experience with wire loop DSI for liquids [11] had shown that when the wire starts deforming it soon either melts or breaks and usually lands on the torch, often cracking it, so it should be promptly retracted and replaced.

Immediately after the insertion of the pellet, sharp peaks were recorded at the Fe and Mn channels. These were soon overtaken by a very intense broad hump. This same hump appeared at every channel and had an unusual wavelength profile. Two individual slices across the time profile of the signal at the channel of Pb after the insertion of a pellet of 1:8 PACS-1 in graphite are overlayed in Figure 5. The first wavescan labelled signal was extracted from the early part of the time profile, during the peak of Pb, and the second wavescan labelled interference was extracted from a later part of the exposure, during the stray light's broad hump. The time profile of this baseline interference is highly correlated with the signal of silicon, as illustrated in Figure 4. Stray light is a prevalent problem in the analysis of geological materials by emission techniques [20], and is especially likely for samples with large concentrations of elements with very intense lines like Ca, Mg, Na and Si.

The wavelength profile of stray light is not well characterized [21]. Usually stray light appears as an increase in the continuum background, but it can also have a strikingly line-like profile when it originates in the secondary optics of older spectrometers, from reflections and scattering in the exit slit assembly [22]. The usual correction for stray light is to block out the excess light striking the spectrometer's entrance slit with an appropriate filter [21]. In most applications, this solution is probably justified by the inherent lack of information in that signal. With DSI however, the onset of the silicon phase is an important feature of the burn, and the stray silicon radiation becomes a convenient marker that should not be filtered out but instead used as a diagnostic tool.

Of the nine other channels observed (Al, Ca, Co, Cu, Cr, Mo, Ni and V; see Table 3 for concentrations in PACS-1) only calcium had a signal that could be distinguished from background noise. The early part of the time profile of calcium's signal could not be resolved from the slow decay of the stray light, but it was clearly associated with the purple and pink emission. The signal at calcium's channel peaked about three minutes after the insertion of the pellet, right when the plasma glowed its brightest pink, and was still going strongly when the pellet was retracted eight minutes after its insertion. The absence of signal for some of the other elements did not come as a surprise, based on the volatility series derived earlier with powdered arc standards [6,14]. Aluminium is probably present as a polymeric oxide which is extremely refractory [23]. Chromium, molybdenum and vanadium on the other hand are all high boiling elements which form thermally stable metallic carbides. There is a range of possible stoichiometries for these compounds, often two or three carbides coexist at the same temperature, and the volatilization of these elements is not favoured [23].

The signals of cobalt and nickel had been difficult to observe even with the g-standards, and it was not surprising that a noisier background would make their detection even more difficult. However, it was disturbing that the signals of silver and copper could not be detected. These elements are present in PACS-1 at concentrations well above their detection limits in the powdered arc standards. Furthermore, because they belong to the categories of volatiles and intermediates, their signals are usually sharp and easily identified. Matrix effects were virtually ruled out for copper based on article by Brenner et al. [8], which reported the successful determination of copper and zinc in geological matrices by DSI.

Visual observation of the plasma after the insertion of the pellets suggested a more likely explanation. The absence of walls on the probe results in a flooding of the plasma by the major constituents of the sample's matrix, as evidenced by the orange emission of silicon infusing the whole discharge. Such a sudden massive release of material is bound not only to affect the thermal contact between the plasma and the probe, but even to modify the chemical composition of the plasma itself. Under these conditions, only elements present in high concentrations (Al, Ca, Fe and Na), or with very intense lines, would be expected to emit signals strong enough to be discerned against the high background over which they appear. The advantages expected from a closer contact between the sample and the plasma with a wire loop support were outweighed by the failure to confine the analyte vapor. This was a disappointment after the excellent performance of this type of system with graphite based arc standards [14].

Insertion of Pellets of Sediment in Graphite Cups

By keeping the escaping vapors confined within a central channel in the plasma, it should be possible to prevent the physical/chemical alteration of the plasma. The support of the pellets was revised once more, and graphite cups were used to hold the entire pellet and prevent the escape of gases from the sides of the probe. With this arrangement, it was now possible to push the sample directly into the plasma without extinguishing it, provided the pellets had been baked in a 130^{o}C oven for at least four hours.

The insertion was best done in one swift motion, deep into the plasma. Then, the plasma was pushed up briefly but settled back down rapidly and anchored itself under the base of the cup. This was another reason for using undercut electrodes, which have already been reported advantageous in terms of detection limits [24,25,26]. Briefly, the maximum temperature of the graphite cup attained depended mostly on the diameter of the stem (cf. Figure 2). Narrower stems resulted in higher cup temperatures [24], which in turn improved detection limits and prevented memory effects. Also, we had found with the powdered arc standards that the signals' peak intensities were considerably enhanced when the fireball could reform around the pellets' base. Likewise, when a graphite cup was used to carry pellets of sediment, it was important that the fireball reform under the base of the cup. Otherwise, the walls of the cup were not sufficient to keep the escaping vapors from invading the plasma's body and a central analyte channel could not be maintained. When the insertion was deep enough that the plasma reformed around the probe's stem under the cup, the plasma looked much as it did when a conventional graphite cup was inserted. Although a bright flash of silicon emission was again observed, it was now confined to a central channel.

A dark central channel was formed in the plasma above the cup's well during the short time it took for the probe to heat up to the decomposition temperature of the silicate matrix. The signals of the very volatile elements (As, Hg, Cd, Pb, Se, Sn and Zn) appeared during this short interval on an almost flat baseline. The peaks were considerably more intense than they had been with the wire loop support, due to the more favorable excitation and observation conditions that resulted from the analyte's confinement in the plasma's central channel. The signals of less volatile elements, like Cu and Mn, appeared during this period over a smooth baseline, but they were eventually overtaken by stray light as the silicate matrix began to decompose. The stray light was very difficult to correct, because its wavelength profile was not flat but line-like. As a consequence, it was difficult to resolve the end of the signals of elements of intermediate volatility from stray light. This manifested itself in distinctly poorer precision on these elements' peak area, around 15 to 20 % RSD for Cu and Mn instead of 7 to 12 % for the volatile elements.

The bright flash of silicon emission was well contained in a central channel, and the main body of the plasma remained unaffected. The orange silicon emission plume flares out about 12 to 15 mm above the top of the probe into a turbulent tailflame. It was easy to see with the naked eye that the signal of silicon was again in two parts, a bright flash and a steady slower release. Two hypotheses can be proposed to explain this observation, but they are difficult to confirm due to the lack of information on the mineralogical composition of the standard reference materials and the absence of detailed theoretical or experimental studies on the basic dynamics of the volatilization process of inorganic compounds [27]. There could be two major Si minerals in the sediment's matrix, or else there is a significant difference between the vaporization conditions at the periphery and core of the probe.

Depending on the dilution ratio of PACS-1 in graphite, silicon's orange emission died out between twenty and fifty seconds after it had begun, and the channel was successively filled with green, blue, purple and pink emission. The latter lasted upward of five minutes, at which time the probe was pulled out of the plasma because the torch started to overheat. When the plasma box's door was opened, thereby triggering the system's interlock and extinguishing the plasma, the torch's outer tube glowed an intense white. The burn was never left to proceed to its ultimate completion, because it was felt that the necessary exposure would be too long for any practical routine application. Furthermore, volatilization enhancers can be used to improve the signals of refractory elements. These are elements that either have a high boiling point themselves (i.e. > 2500 ^{o}C) or that occur naturally as compounds with high boiling points.

Apart from Ca, Fe and Si, none of the refractory elements had a signal intense enough to be discriminated from background noise and the stray light. These elements did not come out of the cup during the burn, which was later confirmed by grinding the pellets, mixing in NaF, a volatilization enhancing reagent, and burning the pellets a second time. These experiments will be described later, after the impact of various burn and exposure parameters on the signals already observable has been discussed.

Co-Optimization of Cup Geometry and Plasma Parameters

The insertion of the probe temporarily pushed the plasma up, which brought the bright core into the spectrometer's viewing height and resulted in a sharp increase in background signal at every channel. If the insertion was deep and rapid, the plasma fell back down rapidly and a few erratic spikes prevented the adequate observation only of As, which is a very volatile element that evolves even before the probe enters the plasma. A slower insertion results in a broad decay of the plasma's background emission, which overlaps the rise of the peaks from volatile elements like Hg, Cd and Pb. Karanassios and Horlick [26] have recently reported similar findings for liquid samples in graphite cups and also found that a virtually instantaneous one-shot insertion best resolved these two transient signals.

The depth of insertion cannot be optimized independently of the cup's height and the spectrometer's viewing height. The insertion must be deep enough that the plasma can reform under the base of the cup, to minimize the duration of the initial transient baseline shifts. A taller cup allows more sample to be carried into the plasma at once, but occupies more of the plasma body. Once the analyte has been vaporized, it must travel long enough in the hotter part of the plasma to be fully atomized and excited. When the cup's lip is pushed higher than the top of the plasma's load coil, the analyte is directly released in the plasma's cooler tail where atomic emission usually occurs. This not only entails poorer energy transfer from the source to the analyte, but pushes the optimal viewing height closer to the turbulent tailflame.

Working within the 2.0 kW operational limit we imposed on the Plasma Therm Model HFP2500D RF generator, the effect of plasma power on the shape and intensity of the signals was investigated next. Our earlier work with the powdered arc standards [14] and that of others [8,26] suggested that higher power levels are definitely advantageous. Here too, it was found that higher power levels resulted in sharper and more intense peaks. The appearance time of the signals was also affected by the plasma's power level. The appearance time of less volatile elements, such as Cu and Mn, was more affected by the change in power level. Also, the quiet period before the burst of silicon emission was shorter at the higher power levels. This impaired the observation of the signals of Fe and the three intermediate elements at 2.0 kW. At that power level, the peak of Fe often merged with the stray light hump. Although the stray light interference of silicon could be corrected by a mathematical procedure [28] because its time profile is the same at every channel, its physical and chemical interferences on the signal itself could not be avoided.

In addition to restricting the flow of sample vapors to a central channel in the plasma, the graphite cup's walls provided an additional temperature gradient between the plasma and the sample. Thus, when graphite cups were first used to carry pellets into the plasma the onset of the silicon phase had been delayed by about ten or fifteen seconds. Thicker walls and deeper wells should constitute additional heat barriers that would slow down the transfer of heat from the plasma to the sample and separate signals in time according to boiling points. Ideally, this more intense peaks. The appearance time of the signals was also affected by the plasma's power level. The appearance time of less volatile elements, such as Cu and Mn, was more affected by the change in power level. Also, the quiet period before the burst of silicon emission was shorter at the higher power levels. This impaired the observation of the signals of Fe and the three intermediate elements at 2.0 kW. At that power level, the peak of Fe often merged with the stray light hump. Although the stray light interference of silicon could be corrected by a mathematical procedure [28] because its time profile is the same at every channel, its physical and chemical interferences on the signal itself could not be avoided.

In addition to restricting the flow of sample vapors to a central channel in the plasma, the graphite cup's walls provided an additional temperature gradient between the plasma and the sample. Thus, when graphite cups were first used to carry pellets into the plasma the onset of the silicon phase had been delayed by about ten or fifteen seconds. Thicker walls and deeper wells should constitute additional heat barriers that would slow down the transfer of heat from the plasma to the sample and separate signals in time according to boiling points. Ideally, this could be used to offset the effect of high power levels and delay the appearance of the silicon interference.

Cups with the same outer dimensions but with walls of three different thicknesses (corresponding to wells of 3.18 mm (1/8") i.d., 3.97 mm (5/32") i.d. and a bit less than 4.76 mm (3/16") i.d.) and wells of two depths (6.35 mm (1/4") and 9.53 mm (3/8")) were tested, and it was found that thicker walls had a more pronounced effect on the temporal separation of spectral interferences than deeper wells. Furthermore, it was also found that deeper wells resulted in peak broadening. A cup with walls of medium thickness and a deep well provided the best compromise, as determined by a separation criterion very similar to the resolution factor used in chromatography (R). The measure of separation used here (R') was the ratio of the distance between the two peaks to the width at half height of the first peak, as shown in Figure 9-a). The width at half height of only the first peak was used to calculate R', since it is the most important of the two signals. This is the only difference between the two resolution criteria, in chromatography the widths at half height of both peaks are used to calculate R.

Figure 9-b) shows how the separation between the two peaks is improved when cups with thicker walls are used to carry the pellets. However, a closer inspection of the signals for the 3.97 mm (5/32") i.d. and 3.18 mm (1/8") i.d. cups shows how the improved separation is accompanied by a concomitant broadening of the first peak. Moreover, Figure 9-c) shows how deeper wells (from 6.35 mm (1/4") to 9.53 mm (3/8")) result in broadened peaks for cups with thick walls (3.18 mm (1/8") i.d.). The graph of R' is plotted as a function of the distance between the two peaks in Figure 10-a) and against probe geometry in Figure 10-b). Although the details of the plots varied, the optimal probe geometry was the same for every volatile element, i.e. a 3.97 mm (5/32") i.d. cup with a 9.53 mm (3/8") well. It was also found that the correlation between probe geometry and forward power is important. Figure 11 shows how the combination of wall thickness, well depth and applied power can be used to enhance both the intensity of the signal of

Pb at 220.350 nm and its resolution from two spectral interferences, a direct spectral overlap (Fe 220.346 nm) and stray light (Si).

The loss of sample mass was not taken into account during the optimization of the probe's geometry, because it was first deemed necessary to maximize the temporal resolution of analyte signals from spectral overlaps and the various interferences arising from the sudden release of silicon in the plasma. On the other hand, it has already been reported in this section how increased sample masses are advantageous in terms of sensitivity and sampling statistics. It was found that better results were achieved by increasing the proportion of sediment in the sample mixtures, while keeping the size of the pellets within the restrictions imposed by the optimized cup geometry.

During the initial investigations with pellets held in wire baskets, it had been found that pellets prepared from mixtures of more than 1 part PACS-1 in 8 parts graphite often shattered. When they didn't shatter, the more concentrated pellets cracked and spurted sample into the plasma at irregular intervals, with dire consequences for the signals. A 1:8 dilution ratio barely offset the mass increase from 30 mg for a standard graphite cup [6] to 250 mg, the weight of pellet that is best accommodated by a wire basket support [14]. On the other hand, with the smoother heating rate afforded by thicker walls and deeper wells it was possible to run mixtures twice as concentrated. This cup geometry limited the pellet's weight to 125 mg, but a dilution ratio of 1:5 almost made up for the loss and kept the effective mass of PACS-1 at slightly more than 25 mg.

In summary, when graphite cups were used to carry pellets into the plasma the onset of the silicon phase was delayed by about ten or fifteen seconds. The signals for the very volatile elements (As and Hg) appeared immediately after the insertion of the probe in the plasma. The other volatile elements (Cd,Cu,Mn,Pb,Se,Sn,Zn) appeared shortly after the insertion of the probe, in roughly the same order as they did with dried solution samples and powdered arc standards [6,8,24,26,29]. As a result of the delay before the appearance of the bright flash of silicon emission, the baseline for the signals of these elements was smooth enough to adequately correct with a polynomial fit. The signals of five elements, Cd, Fe, Hg, Mn and Pb, that were obtained after the optimization of DSI and ICP parameters are shown in Figures 12-a) through -e). The peaks are sharp and intense, much like those reported in the literature for liquids and simple solid materials. Figure 12-c) is particularly interesting, because it shows how selective volatilization can be used to advantage in an optimized DSI procedure. In fact, the temporal resolution of the various components of the signal at the Pb channel appears to be good enough for the semiquantitative determination of Fe.

Thermochemical Additives

Various fluorinating and chlorinating reagents have been used to enhance the volatilization of refractory elements, most notably NaF [6,30], but also AgCl, $BaCl_2$ and NH_4Cl [31]. The technique has been used in arc spectroscopy [23] and graphite furnace atomic absorption (GFAAS) [32].

Our first application of thermochemical additives was diagnostic and aimed at determining how much of the analytes had been vaporized in the course of the first insertion. NaF was used to enhance the volatilization of the refractory elements which may have remained trapped as carbides in the pellets during the first burn. It was also used to check whether any Fe remained in the pellets after the burst of Si emission. The stray light interference had made it difficult to determine whether the slow decay of the peak of Fe had indeed returned to baseline. A report on volatilization enhancers in DSI [31] had determined that the addition of thermochemical substances was necessary to achieve complete evaporation of Fe from ceramic powders and graphite samples.

The burned pellets were ground and mixed with NaF in proportions varying from 6 parts ground pellets : 1 part NaF to 54:1 in 4 equal increments, then pressed into pellets again and reinserted in the plasma. A bright flash of yellow emission immediately followed the insertion of pellets prepared from 6:1 mixtures. Few elements, apart from Fe, gave signals that could be resolved from background noise. This suggested that the thermochemical reaction(s) resulting in volatilization enhancement did not occur instantaneously upon insertion of the pellets into the plasma. When an in-situ pre-heat was used to condition these pellets prior to their insertion into the plasma, sharp peaks were recorded at the channels of Al, Co, Cr, Fe, Mg, Mo, Ni and V. From 6:1 to 30:1, the proportion of NaF in the mixtures had little influence on the appearance of the signals. At 42:1 the signals of Co, Cr and Ni were lost, and only an attenuated signal for Fe remained at a ratio of 54:1. No signal was ever observed for any of the volatile elements, dispelling initial apprehensions that some might remain after the first burn.

When blank mixtures of NaF in graphite were run, signals were observed for Al, Cr, Fe, Mg and Ni. The supplier from which the NaF had been purchased provides an elemental analysis for each batch, and it accounted for the presence of Fe and Mg. Al, Cr and Ni could already have been present in the graphite powder or could have been introduced in the mixing and pressing operations. The contamination of the graphite and reagent was a minor problem, because the signals of the elements of interest in the mixtures of burned pellet and NaF were significantly more intense than those of the blanks.

The reports published so far on thermochemical additives by DSI workers have concentrated exclusively on establishing their volatilization enhancing properties. Consequently, the matrices that were used in these studies were simple and on the whole inert: graphite [6,30], ceramic powders [31], and α-Al_2O_3 [7]. On the other hand, sediments are composed primarily of silicate minerals which are not inert to fluorination. Hydrofluoric acid is often used in the acid digestion of geological materials to accelerate the decomposition of their silicate matrix [33].

The insertion of pellets pressed from a mixture of 1 part NaF : 1 part PACS-1 : 5 parts briquetting graphite resulted in an intense flash of yellow and orange light. The plasma was sometimes extinguished and the flash often filled the whole plasma, so that only a small portion of the fireball remained white. The orange Si emission remained for a limited time after the yellow Na emission had died out. In contrast to what had been seen with unmodified sediments, the orange emission was not followed by the usual sequence of green, blue, purple and pink emission, and there was no discernible signal at the calcium channel. The absence of a calcium signal reinforced the previously established connection between the pink emission that appeared late in the burn without thermochemical additives and calcium. This lack of signal suggested that either fluorine enhanced the volatility of Ca or that the sudden rush of Na and Si entrained Ca [34]. The latter explanation is more likely considering that calcium fluoride has a high boiling point (> 2500^{0}C [35]) comparable to that of nickel (2730^{0}C [35]), which is considered a refractory element.

To summarize, it was not possible to determine whether fluorination resulted in volatilization enhancement, but it obviously accelerated the decomposition of the silicate matrix. The plasma was temporarily flooded with silicon and the ensuing bright flash of yellow and orange emission resulted in severe stray light, which temporarily saturated the integrating capacitors of many channels. The background shift and noise due to the stray light overwhelmed any underlying signal. Sodium was a poor choice for counter ion, because it is a volatile element and a strong emitter. No calcium signal was detected after the burst of silicon emission, in contrast to what was seen with unmodified sediment. The most likely hypothesis was that a mechanism similar to carrier distillation was at work. The sudden massive release of Na and Si may not only result in stray light but could also be responsible for a physical interference, whereby analyte atoms are forced out of the pellet and through the plasma.

When it was clear that no adequate signals would be observed for any element using NaF, alternative thermochemical additives were sought. Other fluorinating reagents, such as powdered Teflon, were rejected in favor of chlorinating reagents. The main reason for favoring chlorine over fluorine was that its reaction with Si is not as violent. Reports on the volatilization of Fe in ceramic and graphite matrices [7,31] had already demonstrated that AgCl was a better choice than $BaCl_2$, NaCl, NH_4Cl, BaF_2, $(C_2F_4)n$, NaF or PTFE, in terms of signals and recovery. This was our first choice.

Mixtures of PACS-1, AgCl and graphite in proportions of 1:1:5 were prepared and pressed into pellets, which were then directly inserted into the plasma. The insertion was immediately followed by a bright green (Ag) flash, which was much less intense than the yellow and orange flash with NaF. The analyte plume was well contained in a central channel through the lower part of the plasma, but it rapidly flared out above the top of the load coil. These pellets had to be inserted higher into the plasma than those pressed from unmodified sediment, or some faint green light was observed around the periphery of the fireball.

An in-situ pre-heat step was essential to allow the thermochemical reactions responsible for volatilization enhancement to proceed. Few one-shot insertions resulted in discernible signals for any of the refractory elements. The pellets were pre-heated under the base of the plasma for various lengths of time, and then inserted in one swift continuous motion. The distance from the top of the cup to the plasma and the speed of insertion were varied systematically, and it was found that longer pre-heats with the top of the probe further away from the base of the plasma worked best. Several seconds after the probe reached the pre-heat position, with the top of the cup 4 mm below the base of the load coil, the plasma constricted and grew brighter. The pellet was ready for insertion when the plasma settled back down, about two minutes later, and sharp signals were recorded for many refractory elements. Although signals were seen at the channels of volatile and intermediate elements, they were weaker than before and distorted. The plasma was noticeably quieter with AgCl than it had ever been with NaF, and, although the burn lasted longer, it proceeded more smoothly.

Figures 13 -a) through -d) show the signals that were recorded at the channels of Al, Co, Cr and V for one such insertion. These signals are well resolved from their spectral background, their time profile is smooth and reproducible from run to run with 10 to 15% RSD on background corrected on-line areas. Once the initial green Ag flare had died out, a milder release of silicon followed. During this period, the only signals that were observed were those of other major matrix components (Al, Ca, Mg and Fe). Here again, the proportions of AgCl to sediment could be varied to minimize the interference from the salt's counter ion, while providing sufficient additive that it did not become a limiting reagent. If the proportion of AgCl was sufficient, it was possible to release all of the major elements before the green flare died. On the other hand, the background intensity was high enough then that some channels saturated as they had with mixtures of NaF and sediment. It was found that a proportion of 1:1 AgCl/sediment constituted the simplest compromise that enhanced the signals of all the trace elements of interest, while minimizing the spectral and physical interferences from the counter ion.

Blanks pressed from mixtures of AgCl in graphite were much cleaner than those of NaF. Aldrich, the supplier from which we purchased the AgCl, reports no contaminants observable by ICP-AES. When running blank mixtures of AgCl and graphite, a signal that could be resolved from background noise and baseline drift was only observed at the channels of Al, Cr and Ni.

Three other chloride salts ($BaCl_2$, $CuCl_2$ and NH_4Cl) were tested as volatilization enhancers. It was found that the thermochemical reactions were much slower with these salts than with AgCl. Of all the combinations of pre-heat conditions that were used only a few resulted in volatilization enhancement rather than the vaporization of the salt [18].

CONCLUSION

The procedures developed for sediments provided good signals for elements of high and intermediate volatility, through a combination of instrumental and methodological optimizations. Of particular importance was the co-optimization of the probe's geometry and plasma power. The dilution ratio of the sediment in graphite was found to have a critical impact on the performance of the technique. It was also found that thermochemical additives could be advantageously used to promote the volatilization of refractory elements.

Table 1

Instrumental Components and Operating Conditions

instrumental components

ICP
  Plasma Therm Model HFP2500D
  AMN2500E automatic matching network
Spectrometer
  Jarrell Ash Atomcomp 90750 direct reader, TSL upgrade [17]
    3/4 m. focal length
    2400 g/mm concave grating blazed for 300 nm
    slits : entrance 50 µm
        exit 25 µm
    PMTs : Hamamatsu R300
        Hamamatsu R427
  data acquisition : TSL integrator cards and controller
DSI
  stepper motor driven shaft assembly :
    laboratory built
  stepper motor controller :
    BIG STEPPER
    (Centroid Corp., State College, PA)
      . 4 motor outlets
      . 8 switch inputs
      . on board BASIC
      . serial port (RS-232 communication protocol)

operating parameters

Forward power	1.0-2.0 kW
Reflected power	0-80 W
Tuning	automatic
Plasma gas flow rate	16 l min^{-1}
Auxiliary gas flow rate	2 l min^{-1}
Viewing height	10-12 mm1

DSI parameters

- optimized for volatile and intermediate elements

Pre-heat height	N/A
Pre-heat	N/A
Insertion depth	-2 mm vs. TOL*
Insertion	150 seconds

- optimized for thermochemical additives

Pre-heat height	-4 mm vs. BOL**
Pre-heat	130 seconds
Insertion depth	-2 mm vs. TOL*
Insertion	90 seconds

* TOL : top of ICP load coil
** BOL : base of ICP load coil

Table 2

Details of materials and tools for pellet DSI

Sediment SRM :	
PACS-1	Marine Analytical Chemistry Standards Program National Research Council (NRCC) Atlantic Research Laboratory Halifax, Nova Scotia, Canada
Briquetting graphite powder :	
Spectroscopic Electrodes	Bay Carbon Bay City, MI, USA
Pellet press :	
	Parr Instruments Moline, IL, USA
Graphite cups :	
Graphite rods C-3 MD	Bay Carbon Bay City, MI, USA

Table 3

Concentration of selected matrix and minor constituents in PACS-1 - (percent)

Al_2O_3	12.23
CaO	2.92
Fe_2O_3	6.96
Na_2O	4.40
SiO_2	55.7

Concentration of selected trace elements in PACS-1 - (μg/g)

volatile elements :		
	As	211
	Cd	2.38
	Hg	4.57
	Pb	404
	Se	1.09
	Zn	824
intermediate elements :		
	Cu	452
	Mn	470
	Sn	41.1
refractory elements :		
	Co	17.5
	Cr	113
	Mo	12.3
	Ni	44.1
	V	127

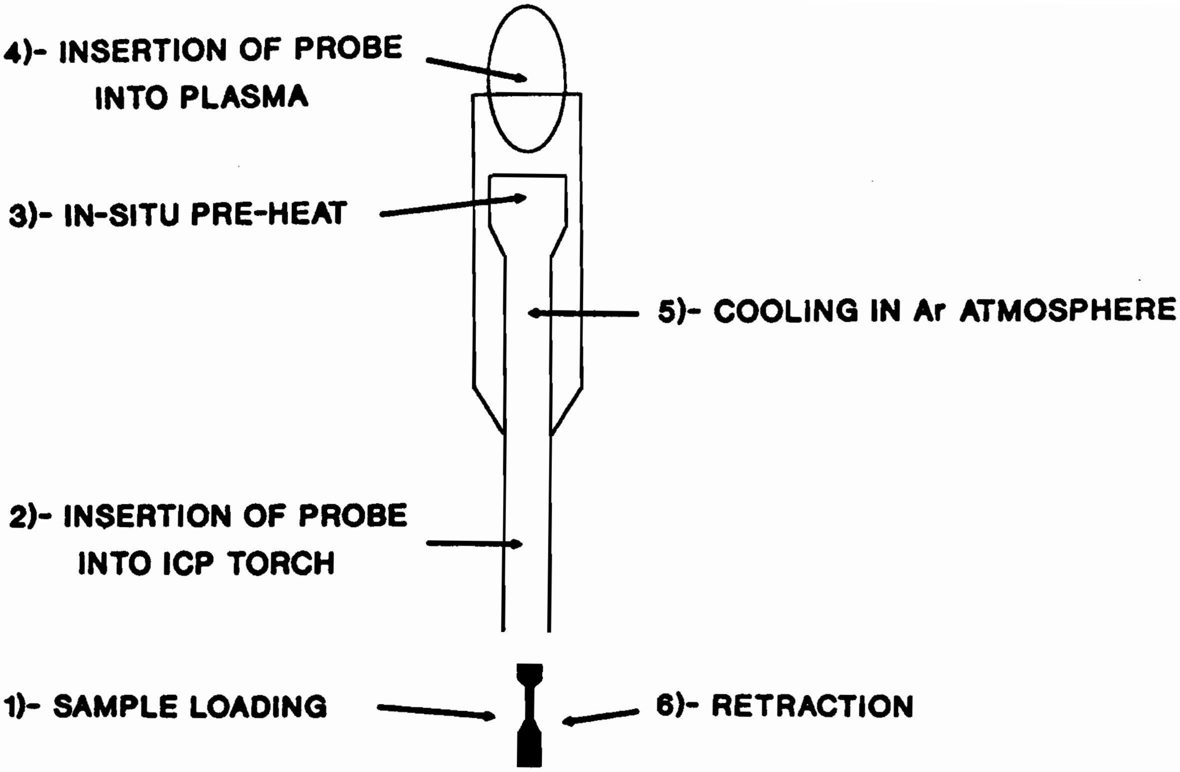


Figure 1
A typical DSI insertion sequence consists of six steps which may be linked to form a continuous smooth motion, or may be separated by various delays.

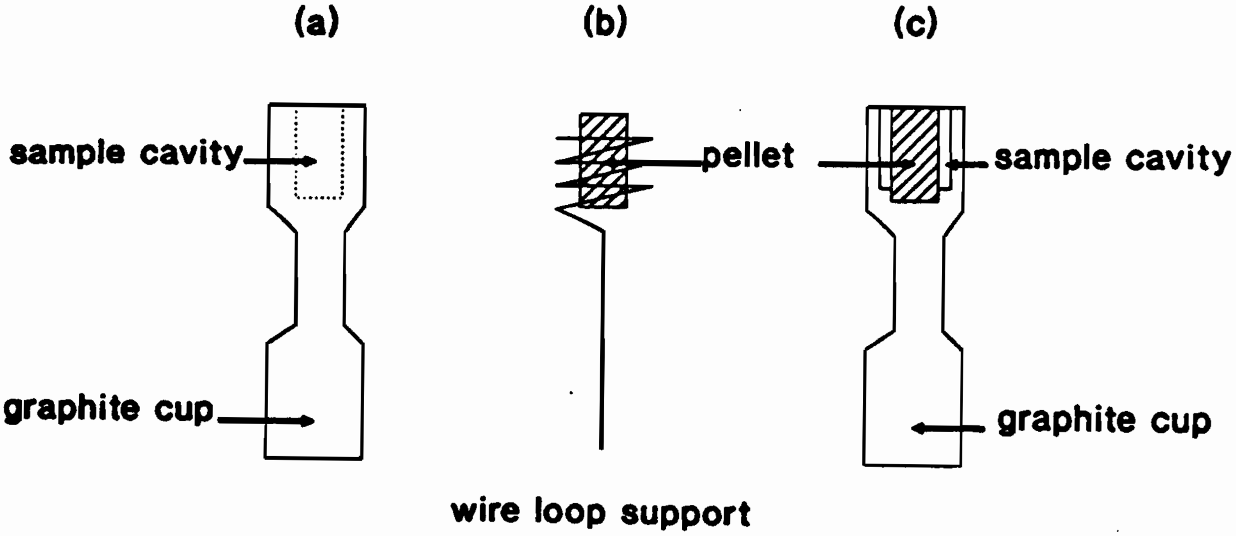


Figure 2
The three types of DSI probes that were used in this work are (a)- a conventional d.c. arc type electrode, (b)- a pellet held in a wire basket and (c)- a pellet held in a graphite cup.

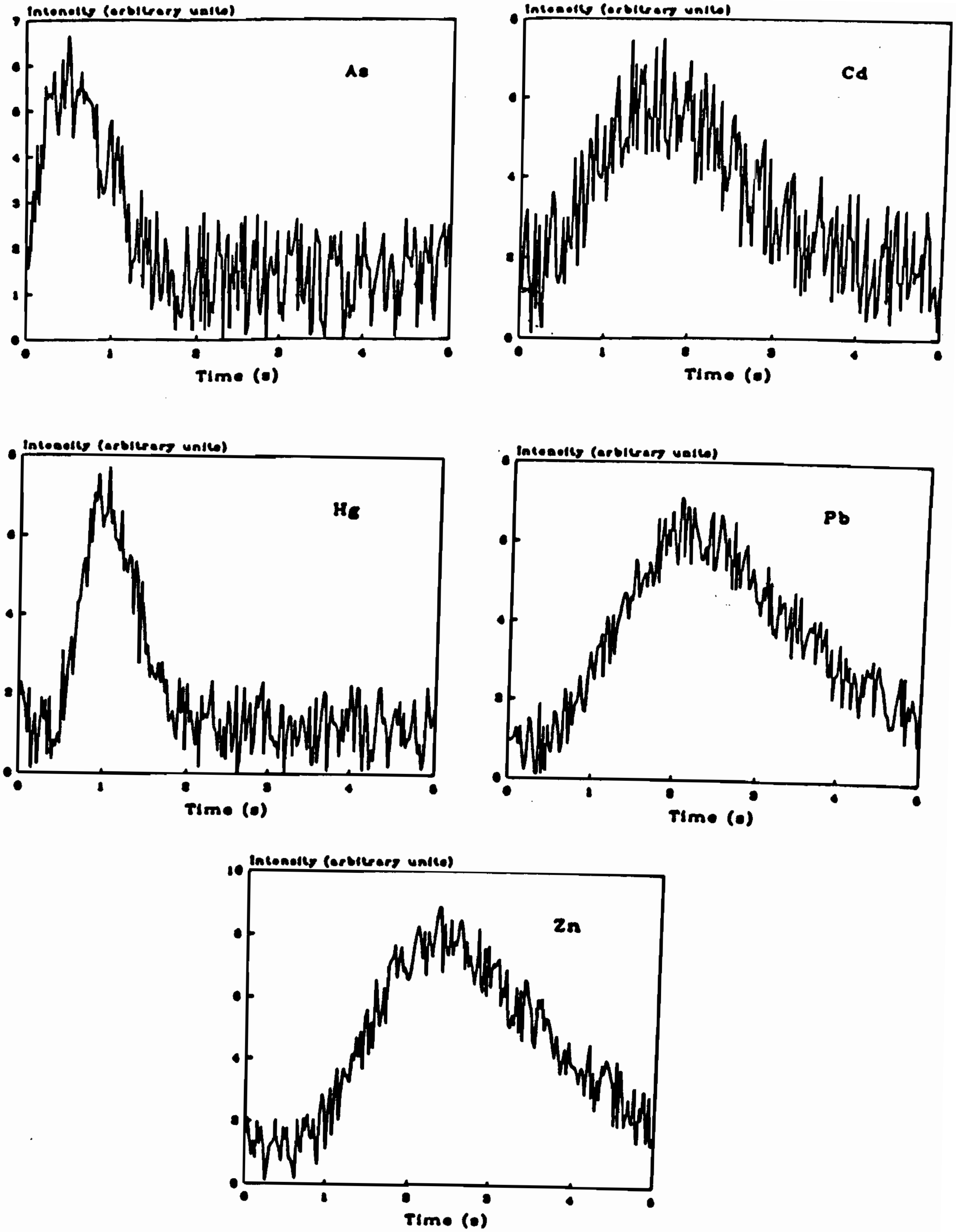


Figure 3

Signals observed at the As, Cd, Hg, Pb and Zn channels during the pre-heat step prior to the insertion of 1:8 PACS-1/graphite pellets held in wire baskets

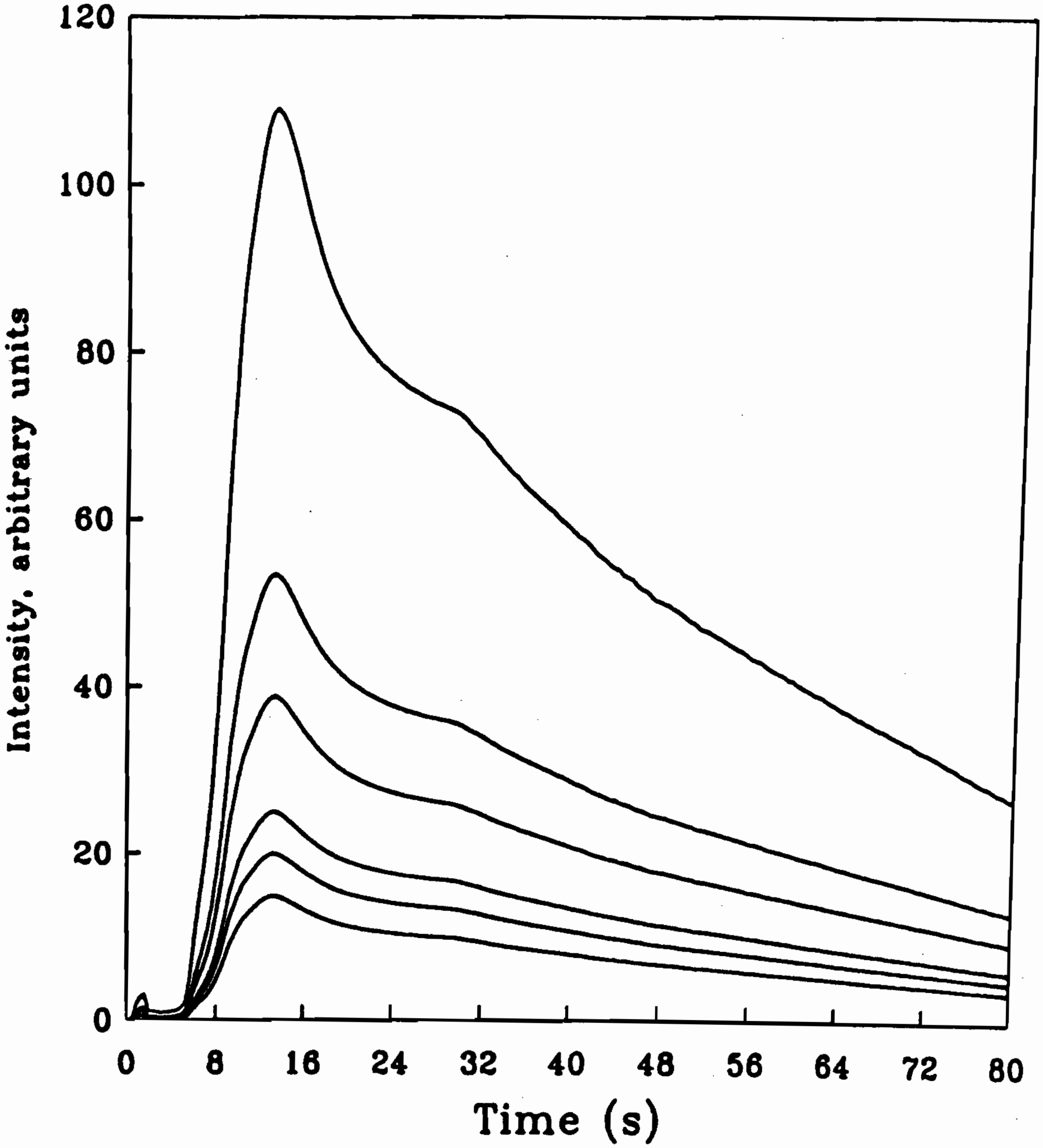


Figure 4

Time profile of the baseline interference observed a few seconds after the insertion of a pellet of 1:8 PACS-1 in graphite at the Hg, Zn, Cu, Pb and Cd channels in ascending order. The top trace is the signal of Si, included to emphasize the correlation of the baseline interference with that signal. The time profile of the signals at the first five channels was recorded with the spectrum shifter set farthest from its on-line position.

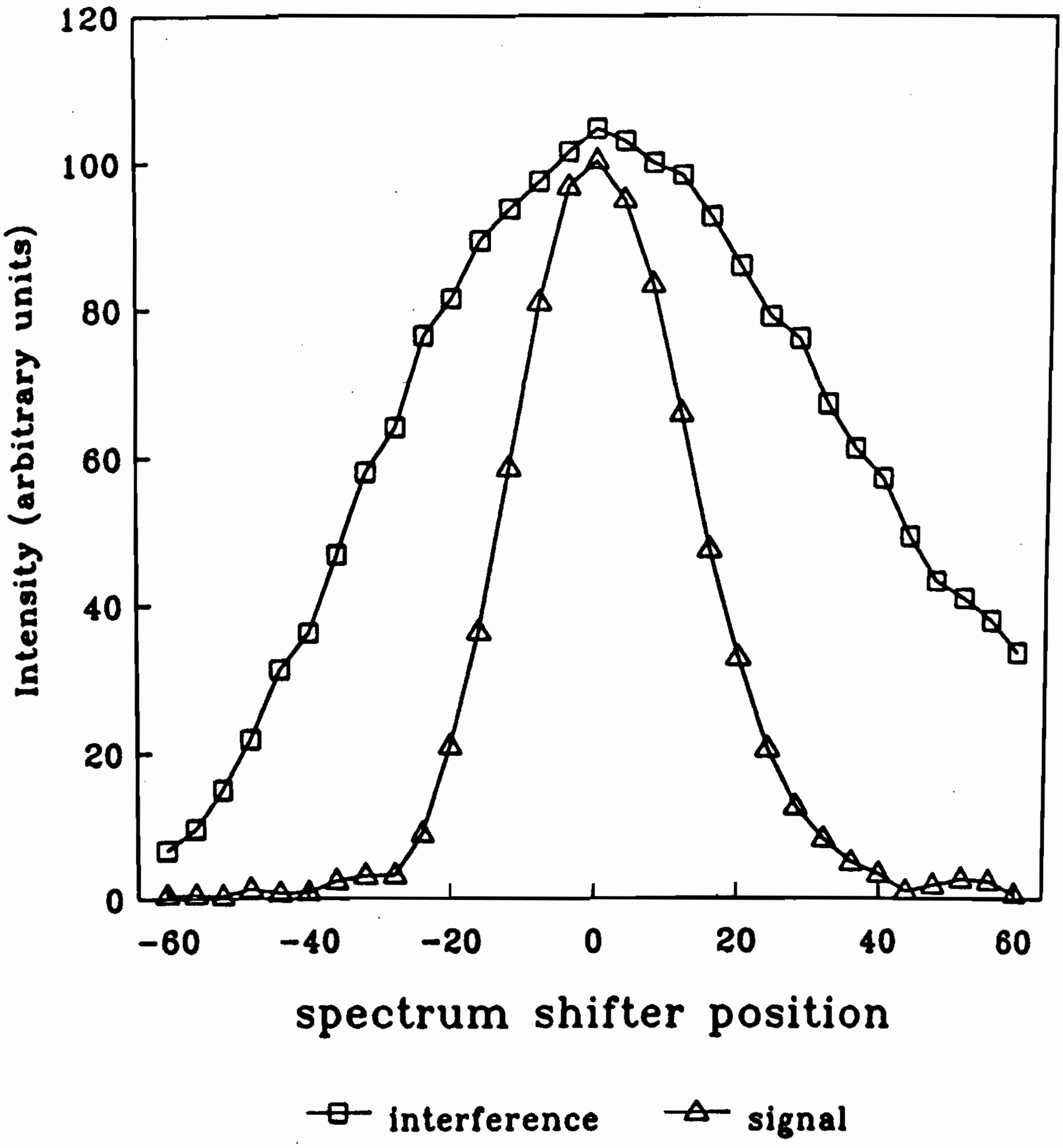


Figure 5

Two slices across the time profile of the signal at the channel of Pb after the insertion of a pellet of 1:8 PACS-1/graphite. One, labelled signal, was extracted from the early part of the time profile, during the peak of Pb. The other, labelled interference, was extracted from a later part of the exposure, during the stray light's broad hump.

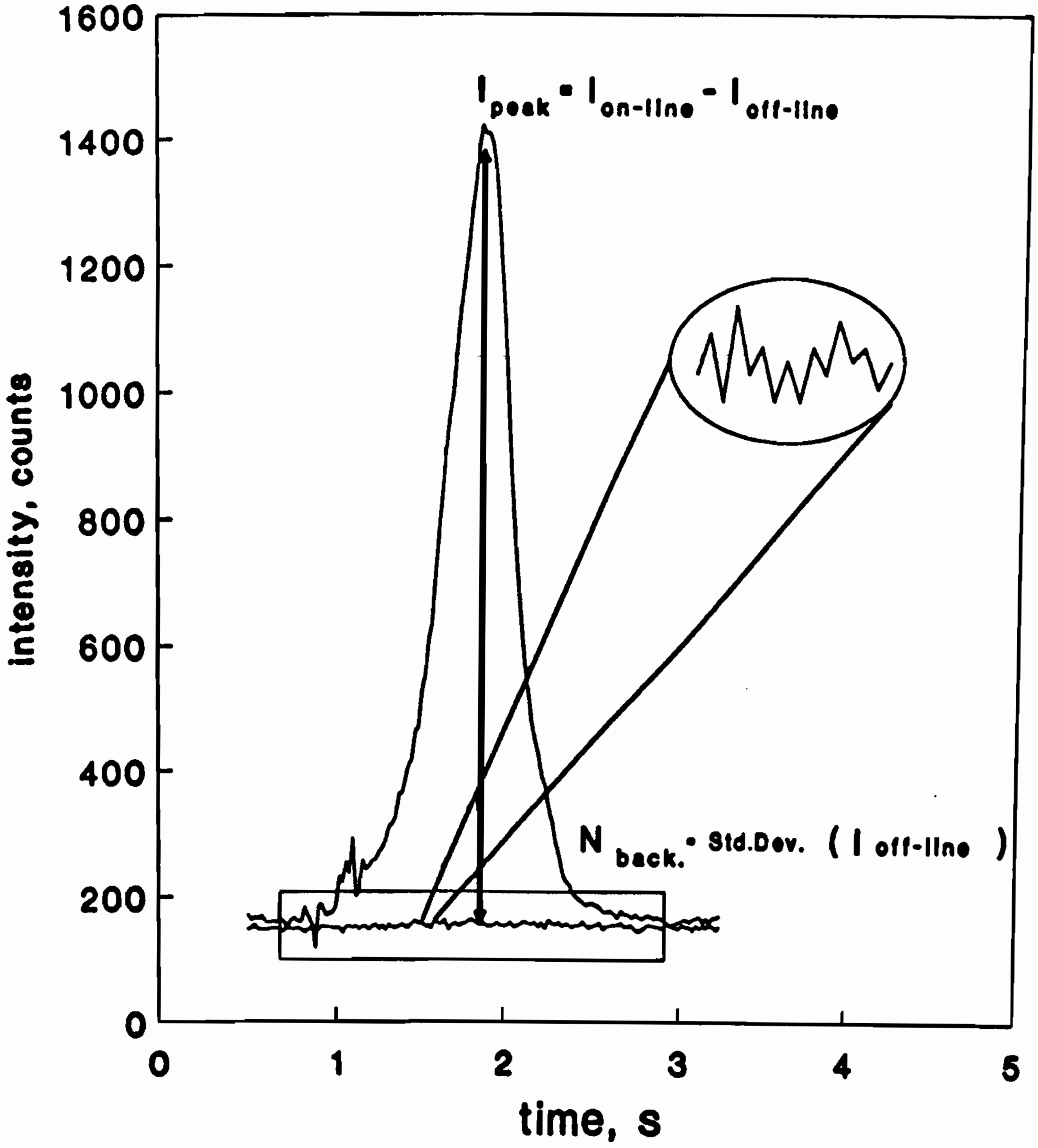


Figure 6

Calculation of the two parameters I_{peak} and $N_{back.}$ from the on-line and off-line signals. I_{peak} is the difference between on-line and off-line intensities at the peak's maximum, and $N_{back.}$ is the standard deviation of the off-line signal calculated over the duration of the peak only (as indicated by the box around the off-line trace).

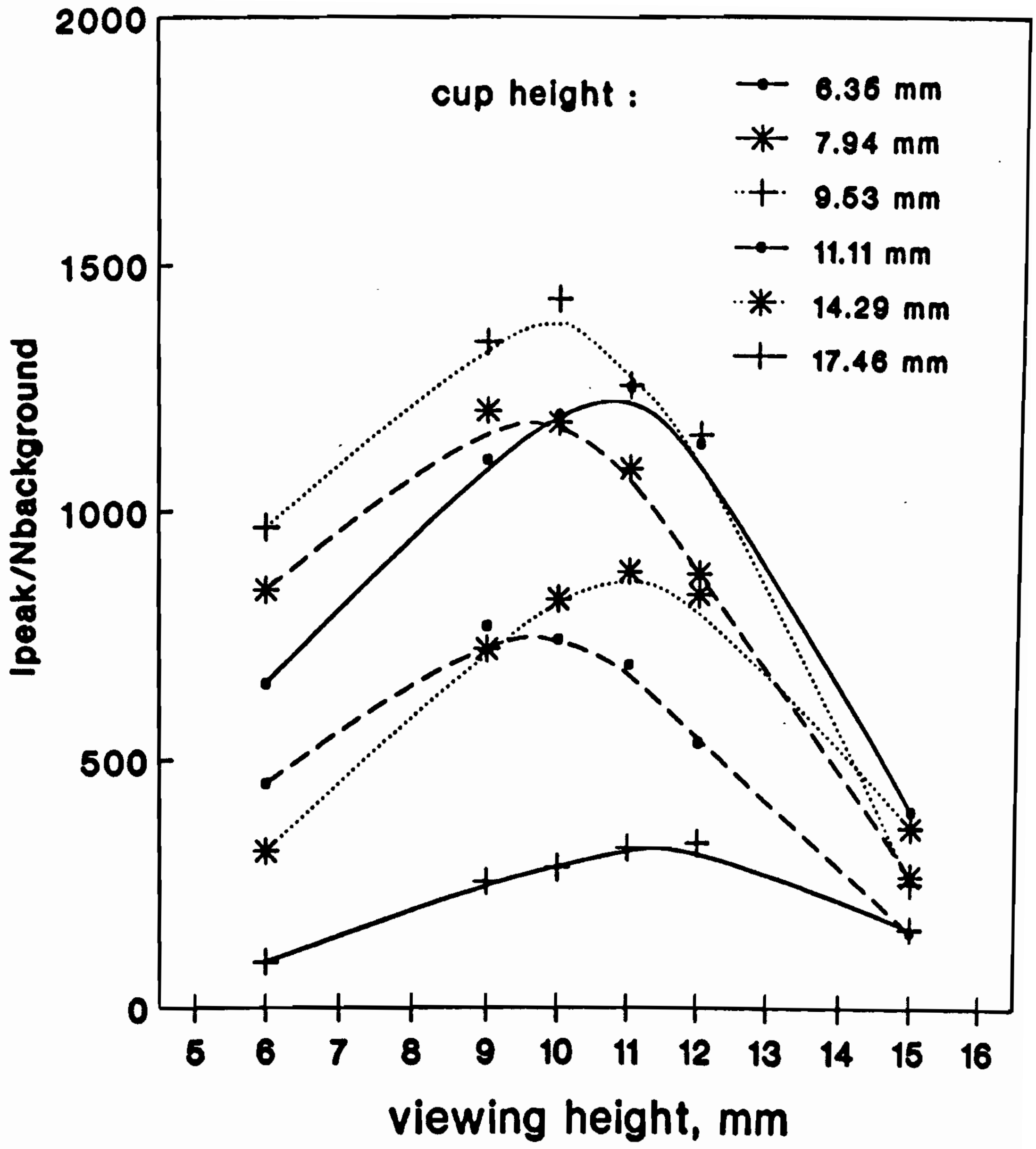


Figure 7

Average ratio of I_{peak} to $N_{back.}$ for Pb, plotted as a function of viewing height for each cup geometry studied.

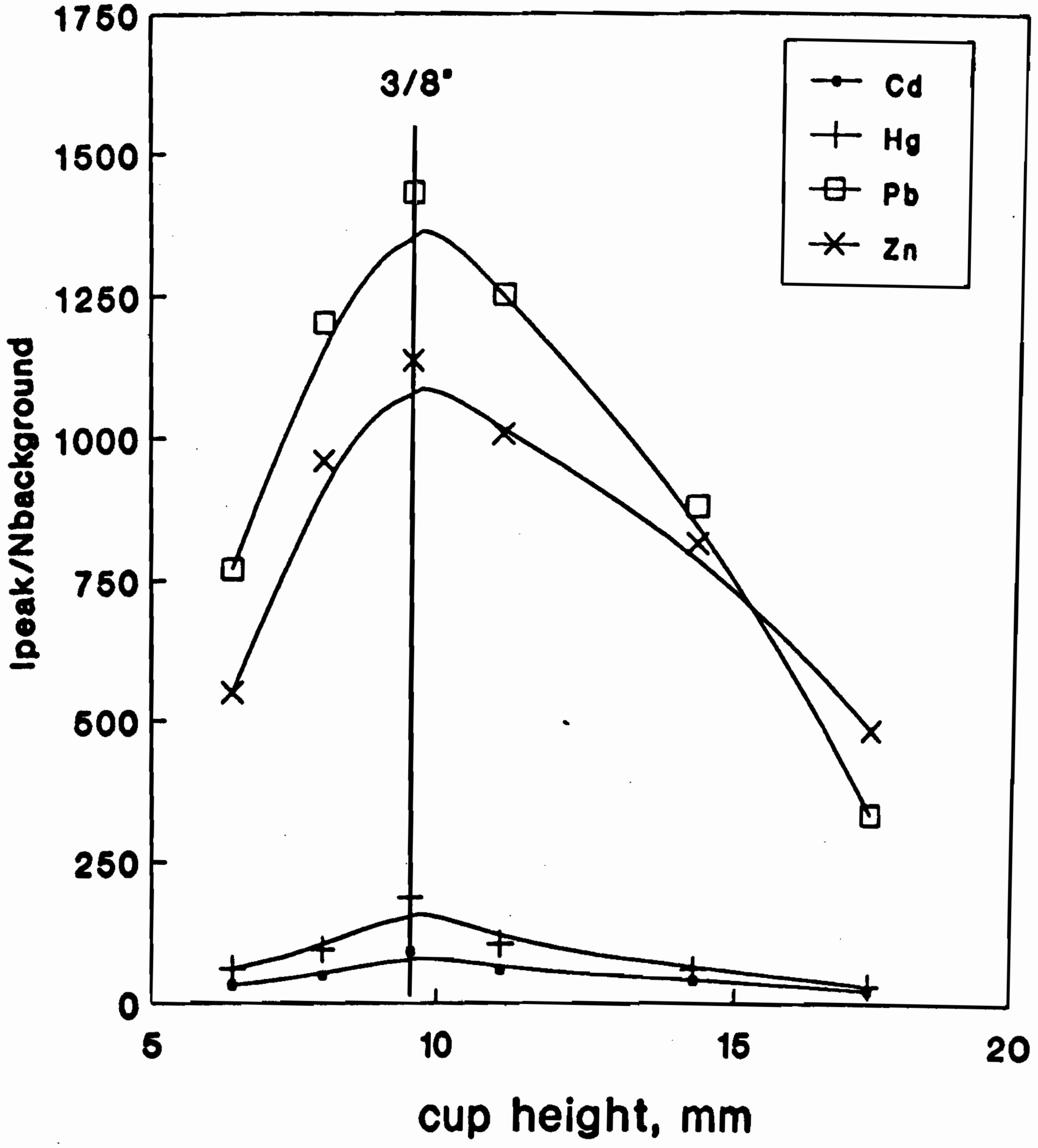


Figure 8
Average ratio of I_{peak} to $N_{back.}$ for Cd, Hg, Pb and Zn, plotted as a function of the graphite cup's height.

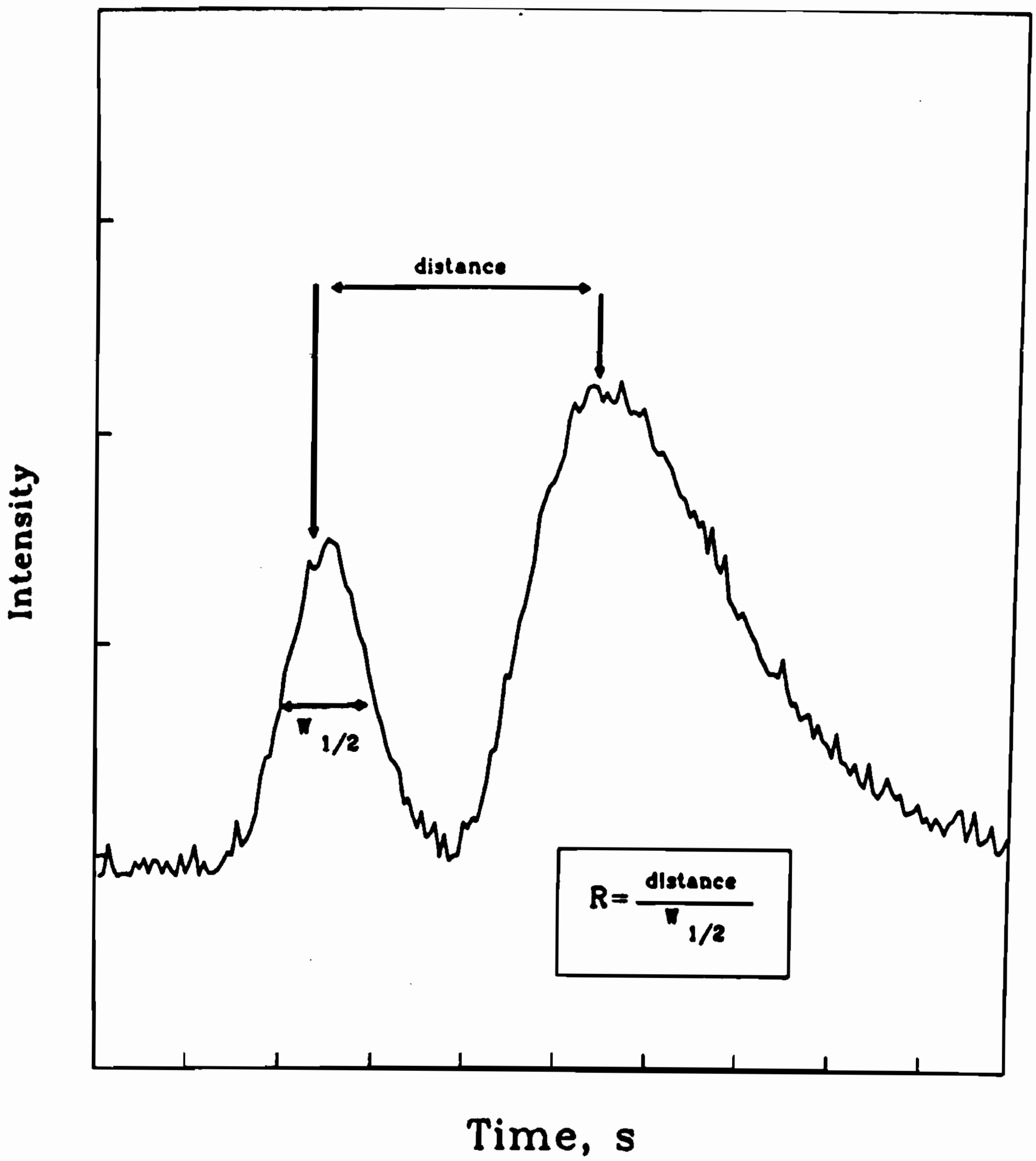


Figure 9.a)-
Calculation of the measure of separation R', the ratio of the distance between the two peaks and the width at half height of the first peak.

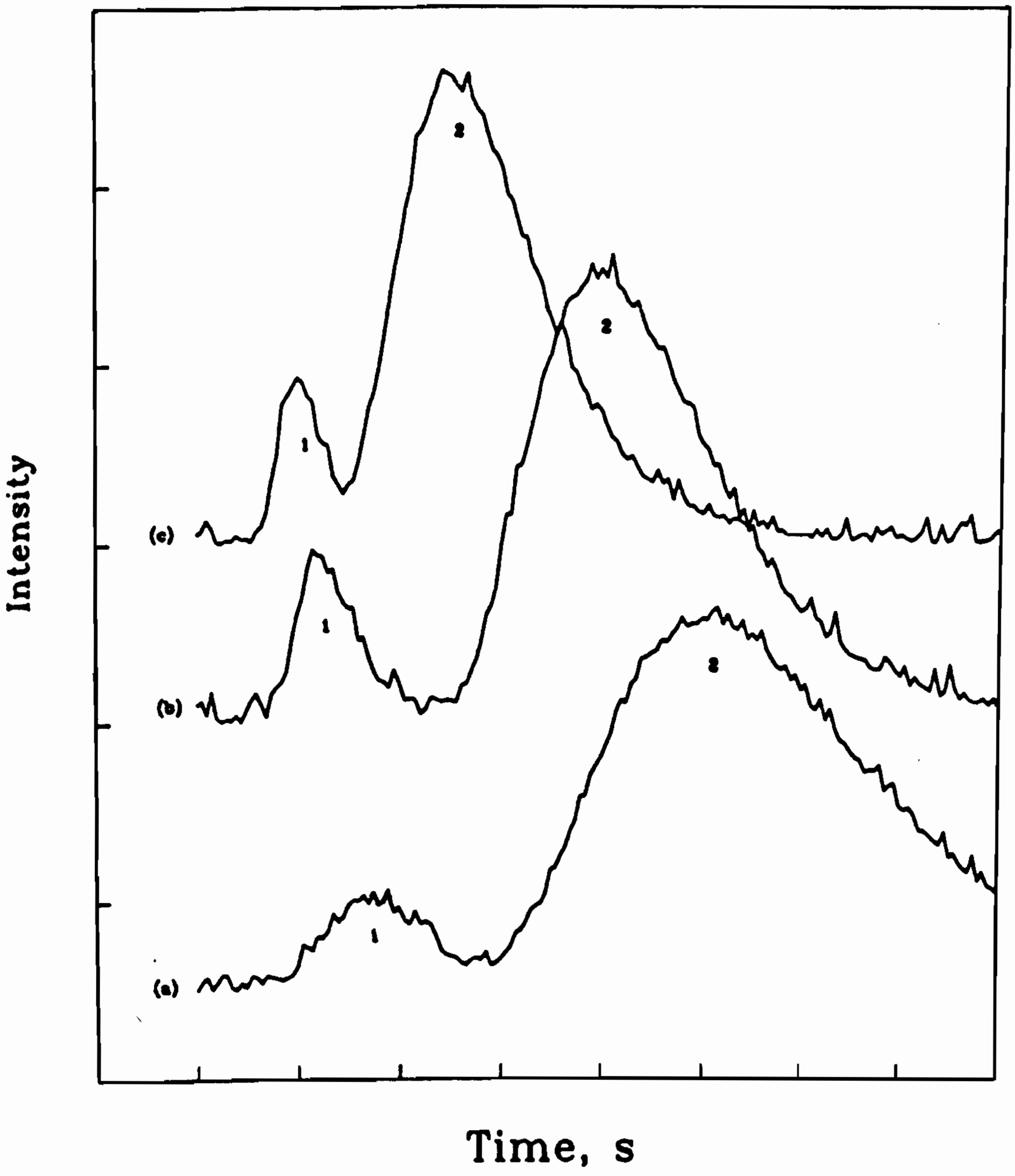


Figure 9.b)-
Effect of the graphite cup's wall thickness on the temporal resolution of the signal of Pb (1) from a spectral interference (2).

Traces : (a) - 11/64" id, 3/16" od
(b) - 5/32" id, 3/16" od
(c) - 1/8" id, 3/16" od

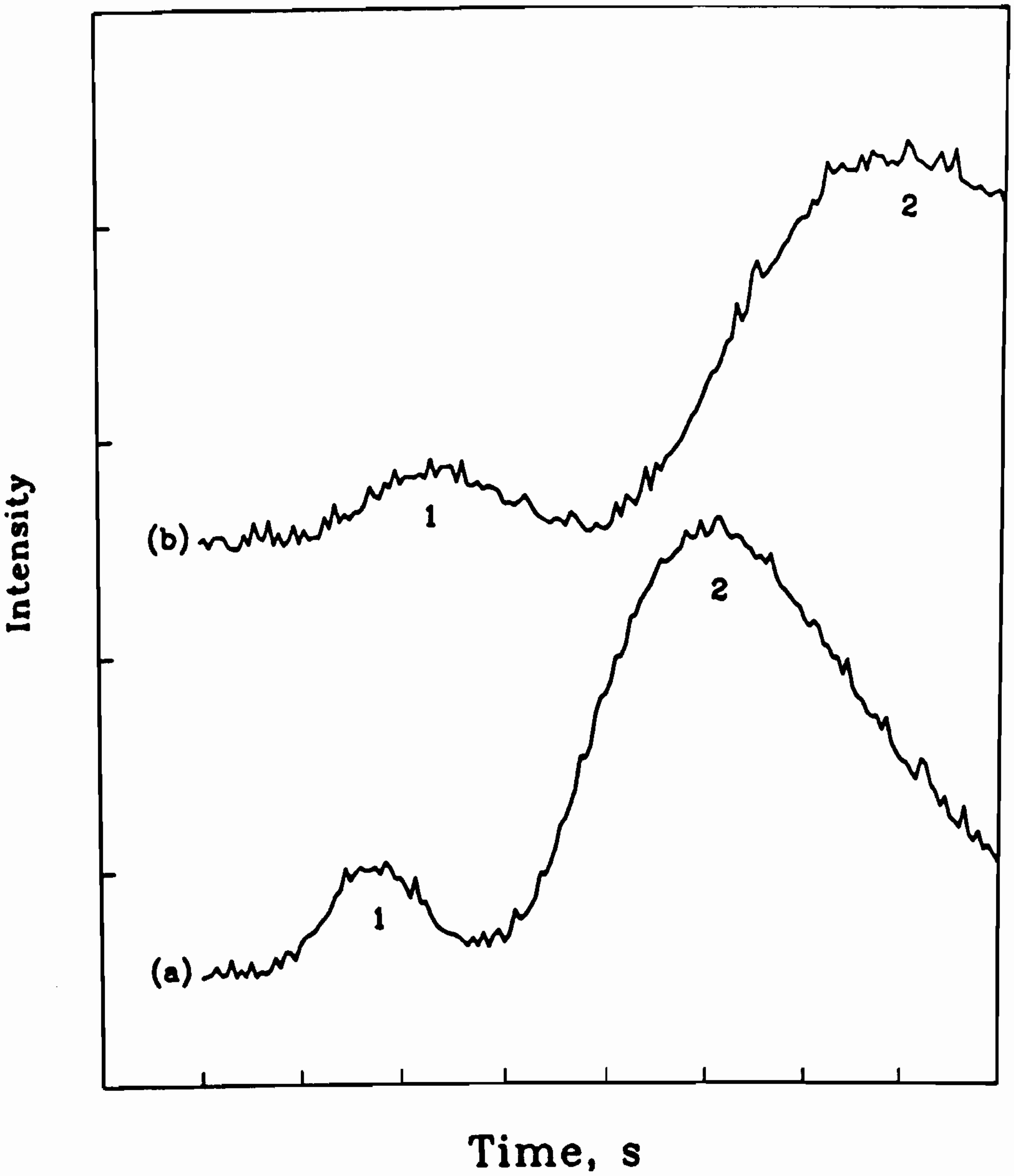


Figure 9.c)-
Effect of the depth of the graphite cup's well on the temporal resolution of the signal of Pb (1) from a spectral interference (2).

Traces : (a) - 1/4" depth
(b) - 3/8" depth

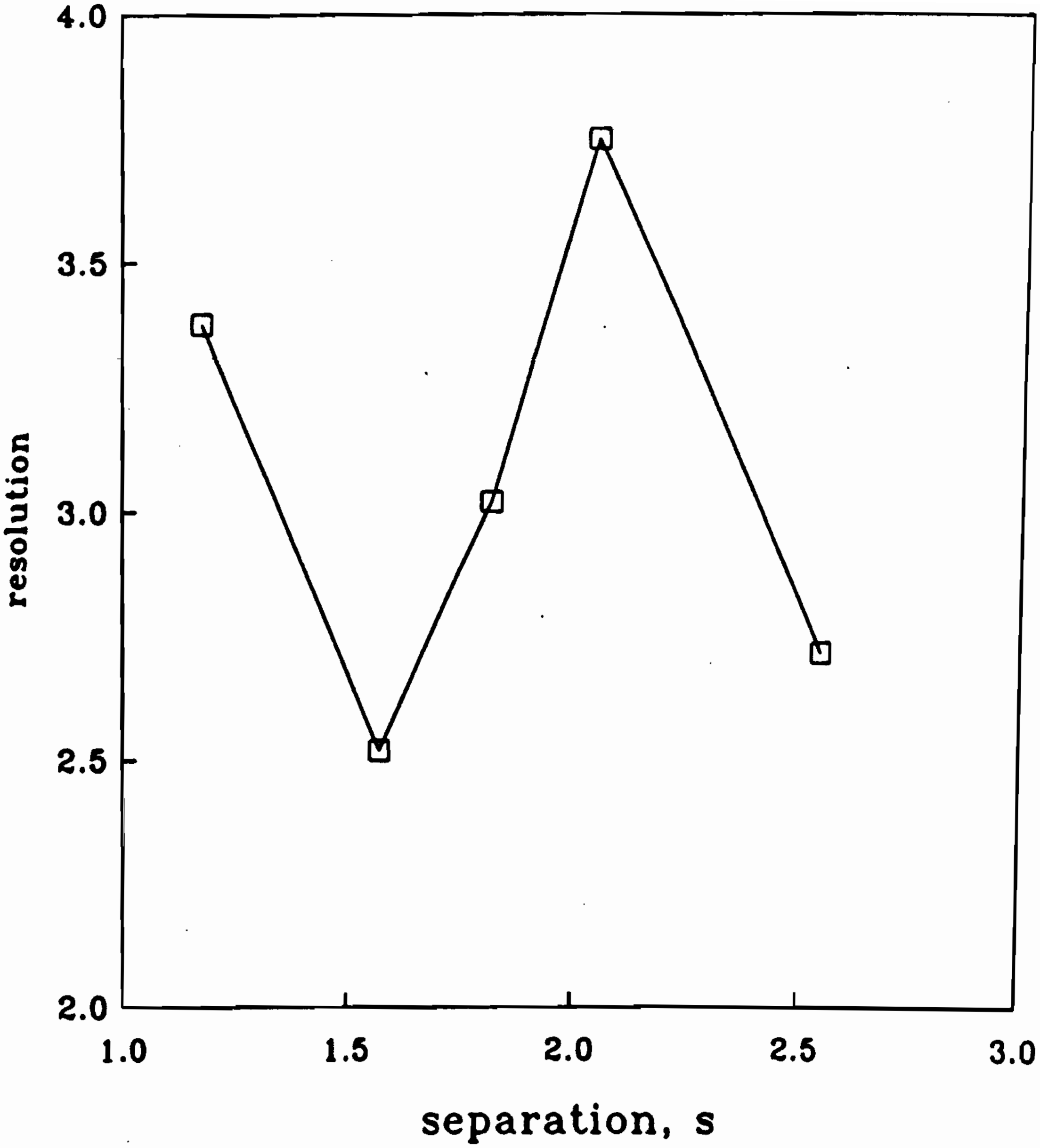


Figure 10.a)-
The measure of separation R' plotted as a function of the temporal separation between the two peaks of Figures 9-b) and 9-c).

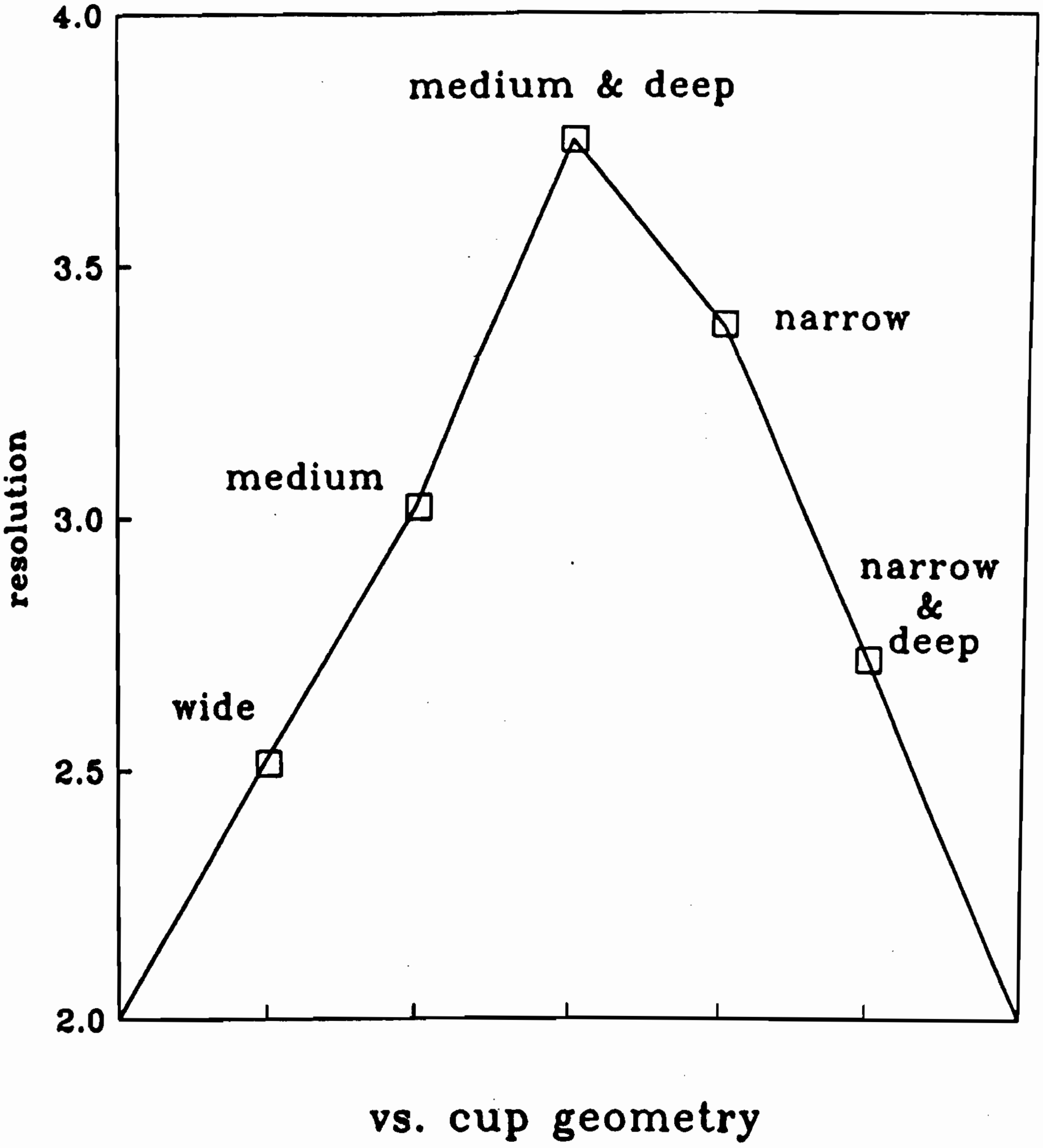


Figure 10.b)-

The measure of separation R' plotted as a function of graphite cup geometry.

Narrow - 11/64" id, 1/4" depth
Narrow & deep - 11/64" id, 3/8" depth
Medium - 5/32" id, 1/4" depth
Medium & deep - 5/32" id, 3/8" depth
Wide - 1/8" id, 1/4" depth

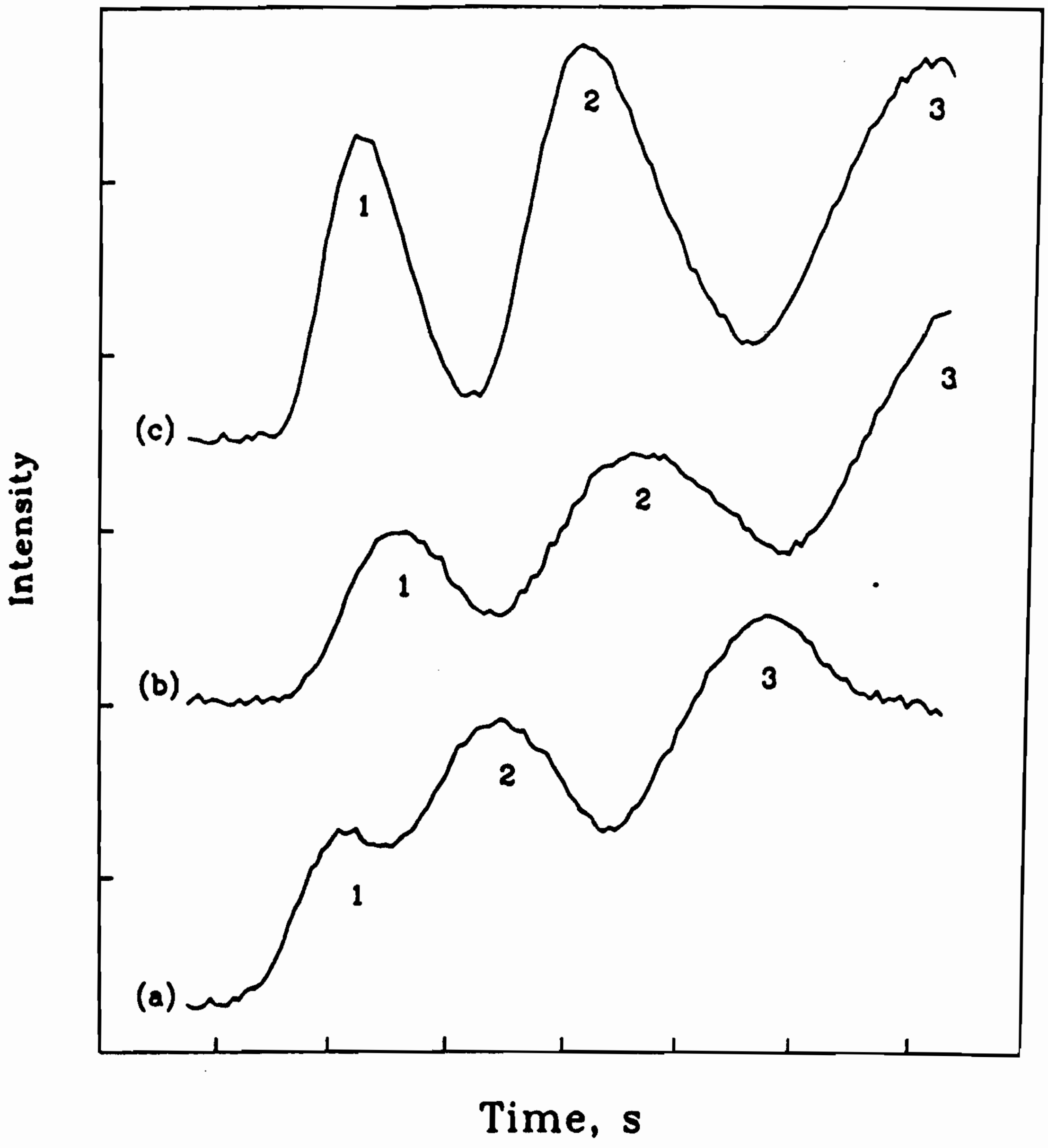


Figure 11

The combined effect of wall thickness, well depth and plasma RF power on the temporal resolution of analyte signal (1st peak, Pb) from a spectral overlap (2nd peak, Fe) and a stray light interference (3rd peak, Si)

Traces : (a) - medium walls, shallow well @ 1.5 KW
(b) - medium walls, deep well @ 1.5 KW
(c) - medium walls, deep well @ 2.0 KW

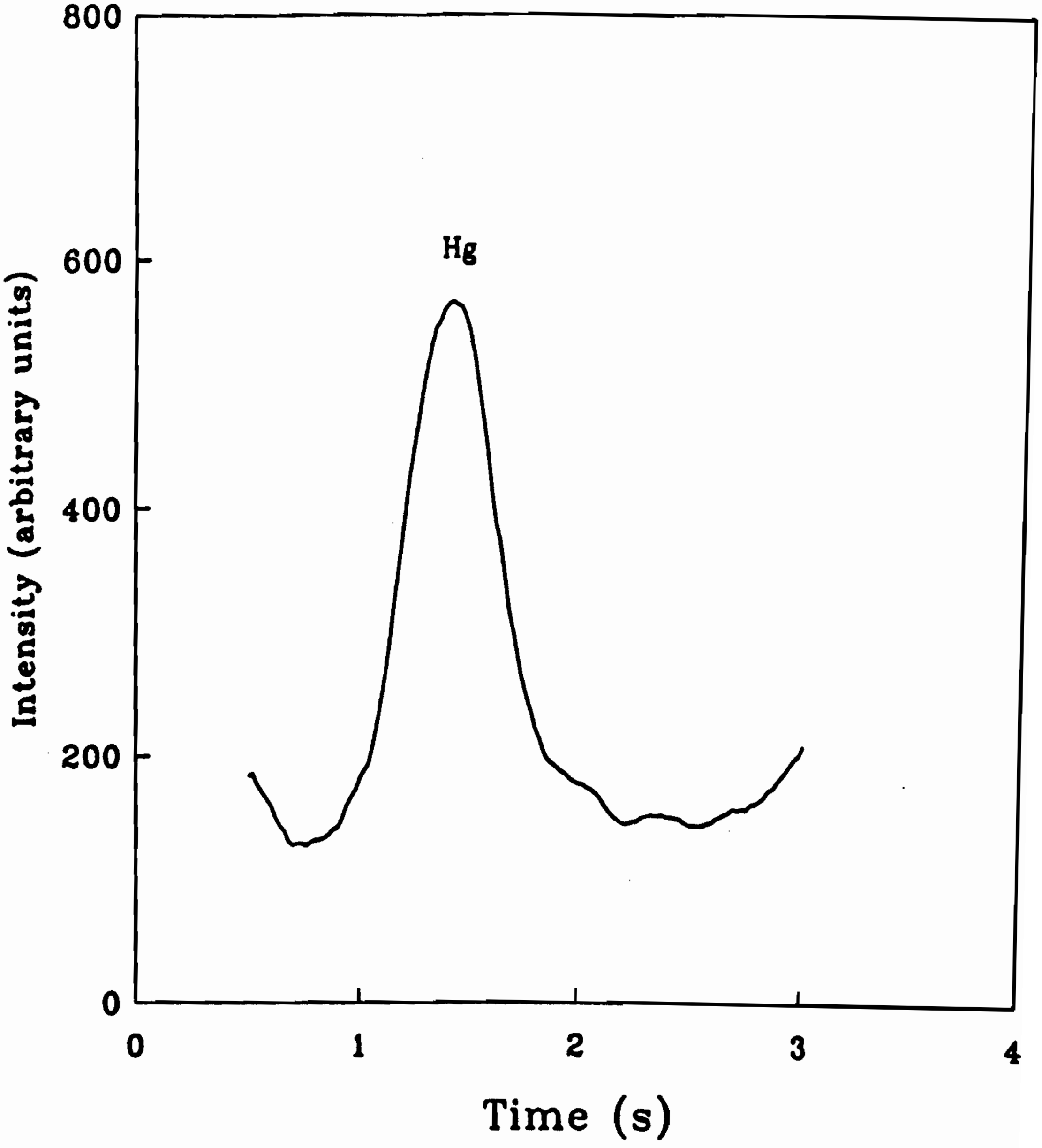


Figure 12.a)-

Signal of Hg after the multivariate optimization of DSI and ICP parameters

probe : 125 mg pellet of 1:5 PACS-1/graphite

category : very volatile

concentration in PACS-1 : 4.57 ppm

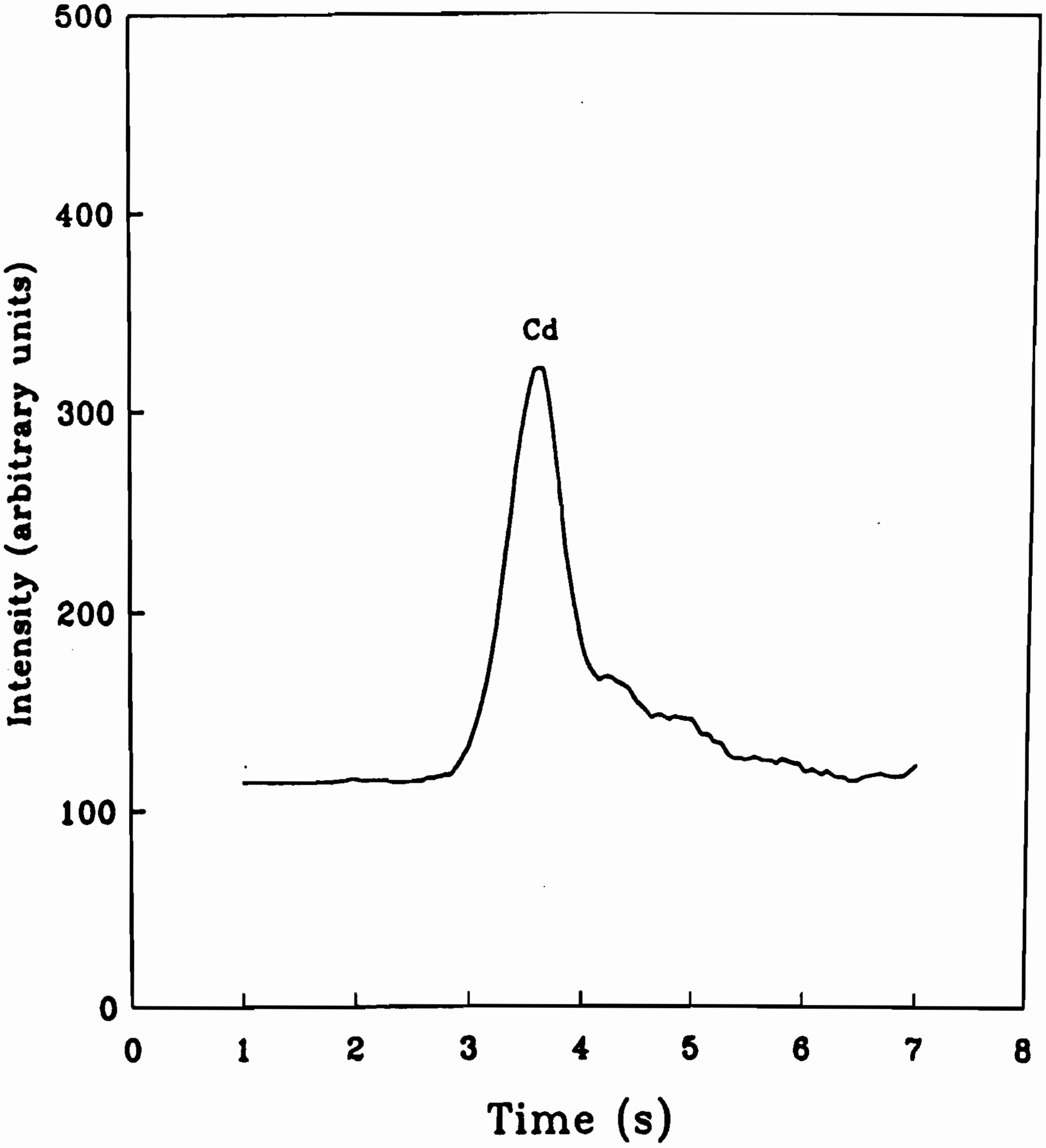


Figure 12.b)-
Signal of Cd after the multivariate optimization of DSI and ICP parameters
probe : 125 mg pellet of 1:5 PACS-1/graphite
category : volatile
concentration : 2.38 ppm

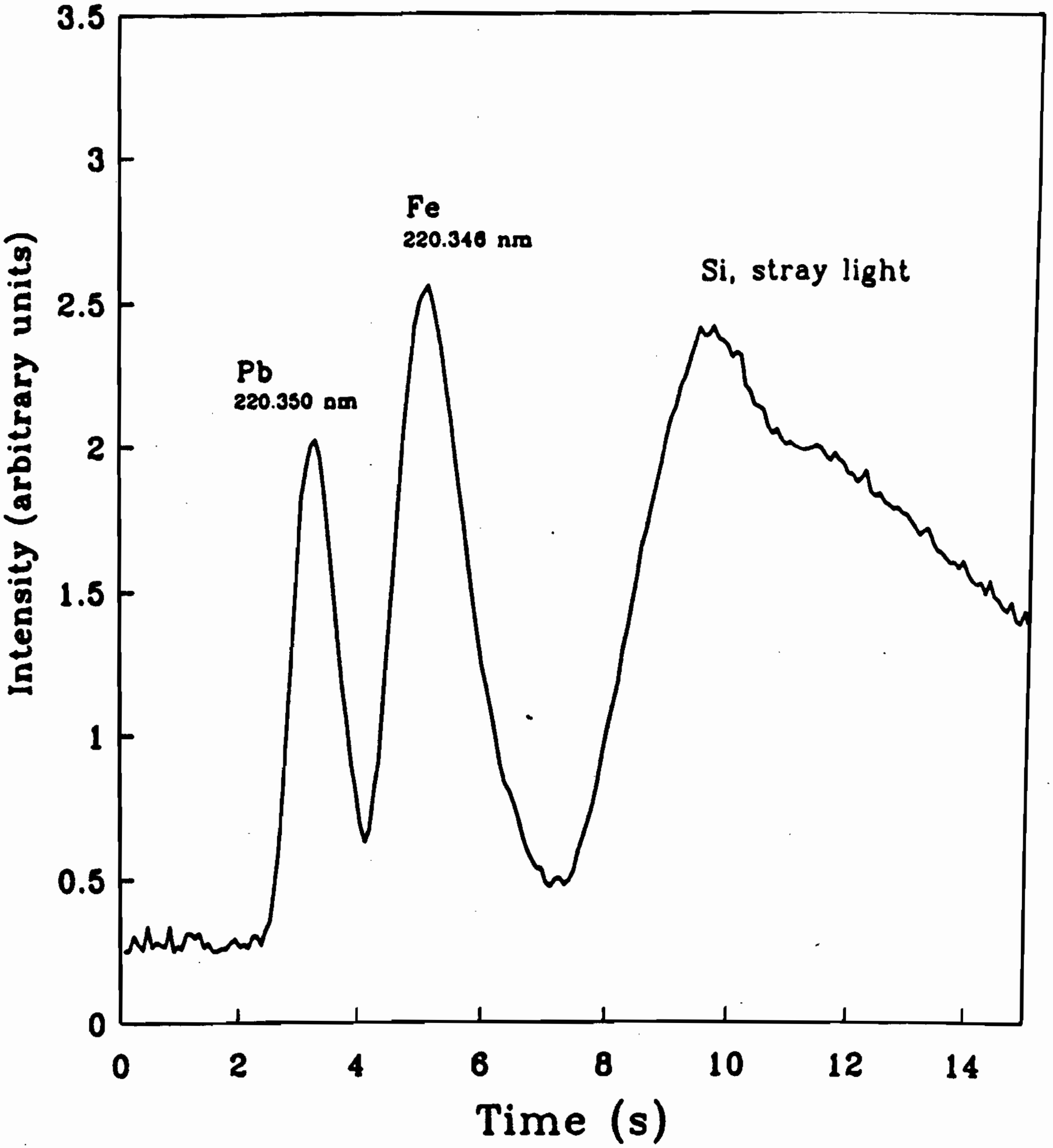


Figure 12.c)-
Signal of Pb after the multivariate optimization of DSI and ICP parameters, illustrating temporal resolution of interferences
probe : 125 mg pellet of 1:5 PACS-1/graphite
category : volatile
concentration : 404 ppm

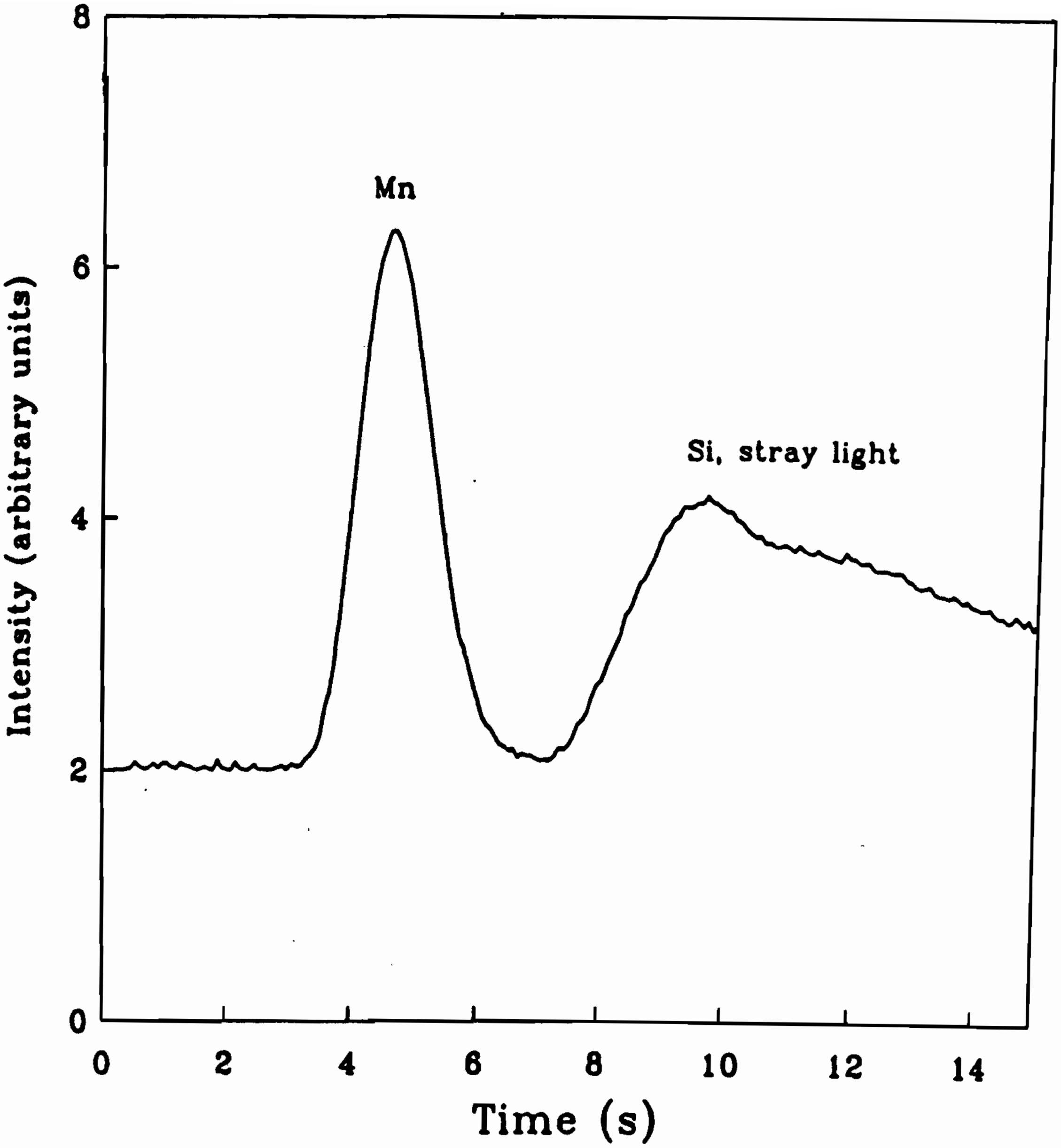


Figure 12.d)-
Signal of Mn after the multivariate optimization of DSI and ICP parameters
probe : 125 mg pellet of 1:5 PACS-1/graphite
category : intermediate volatility
concentration : 470 ppm

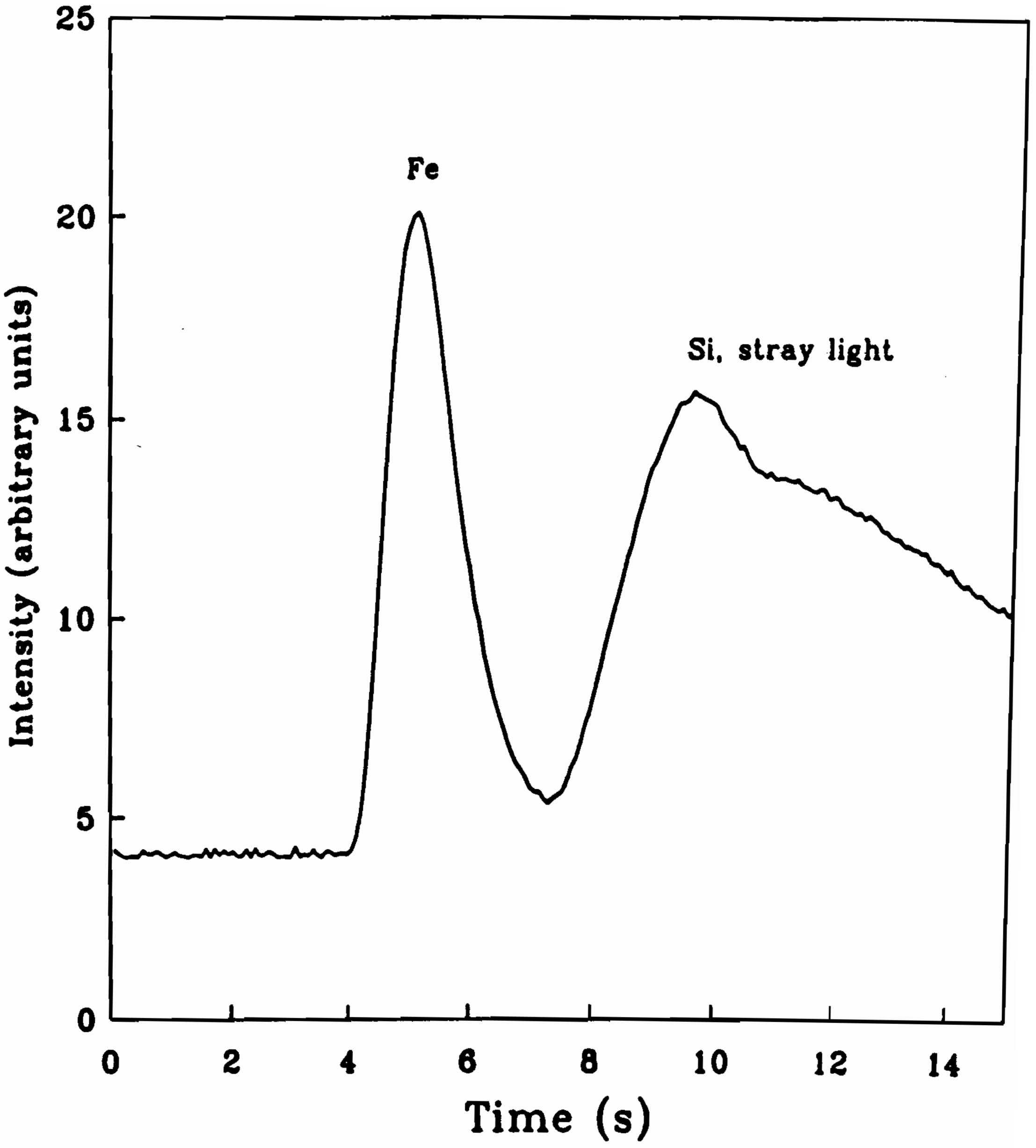


Figure 12.e)-

Signal of Fe after the multivariate optimization of DSI and ICP parameters

probe : 125 mg pellet of 1:5 PACS-1/graphite

category : refractory

concentration : 6.96 %

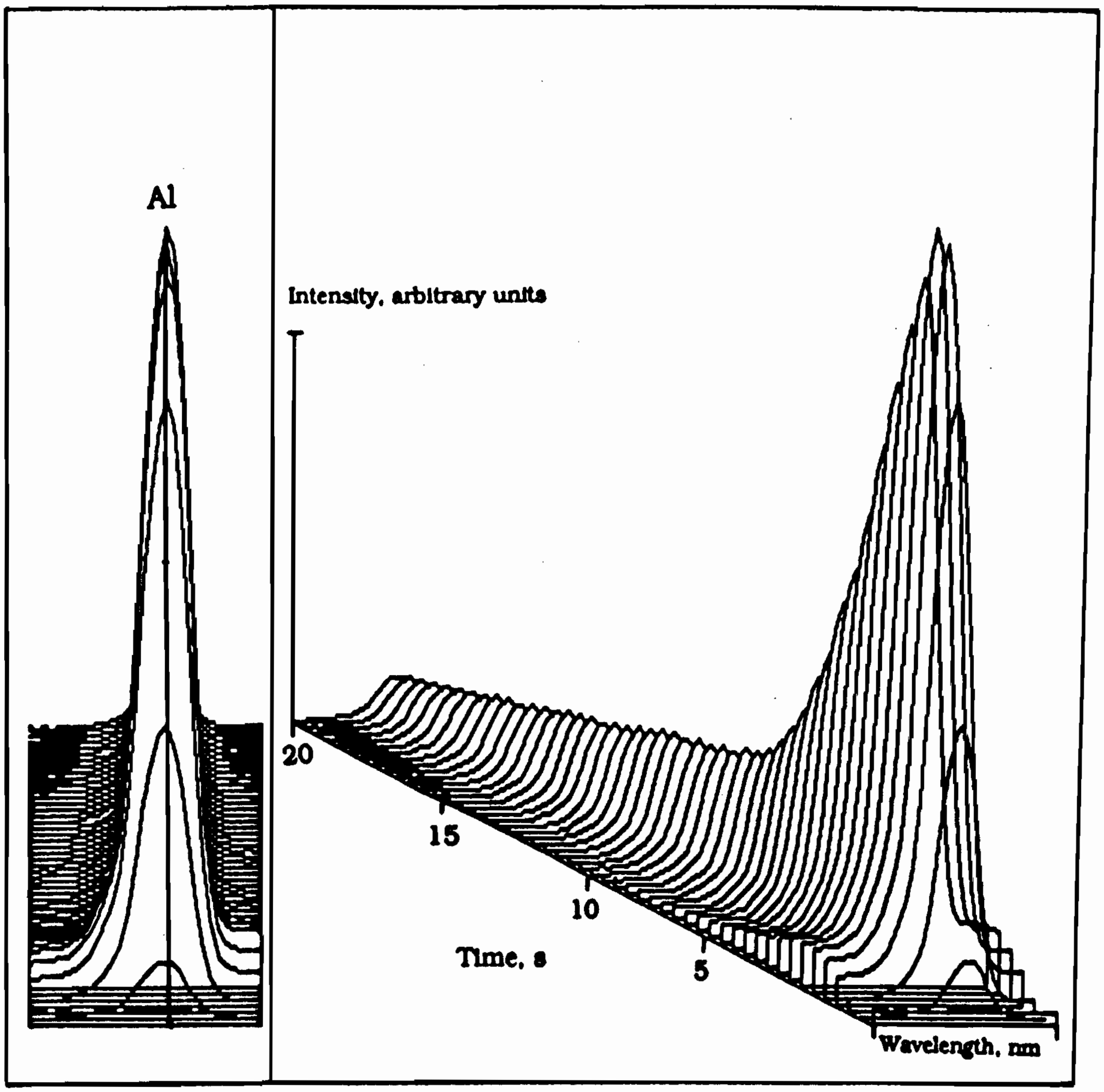


Figure 13.a)-

Signal of Al from the insertion a 125 mg pellet of 1:1:5 AgCl/PACS-1/graphite.
concentration : 12.23 %
wavelength span : 0.064 nm in 32 steps

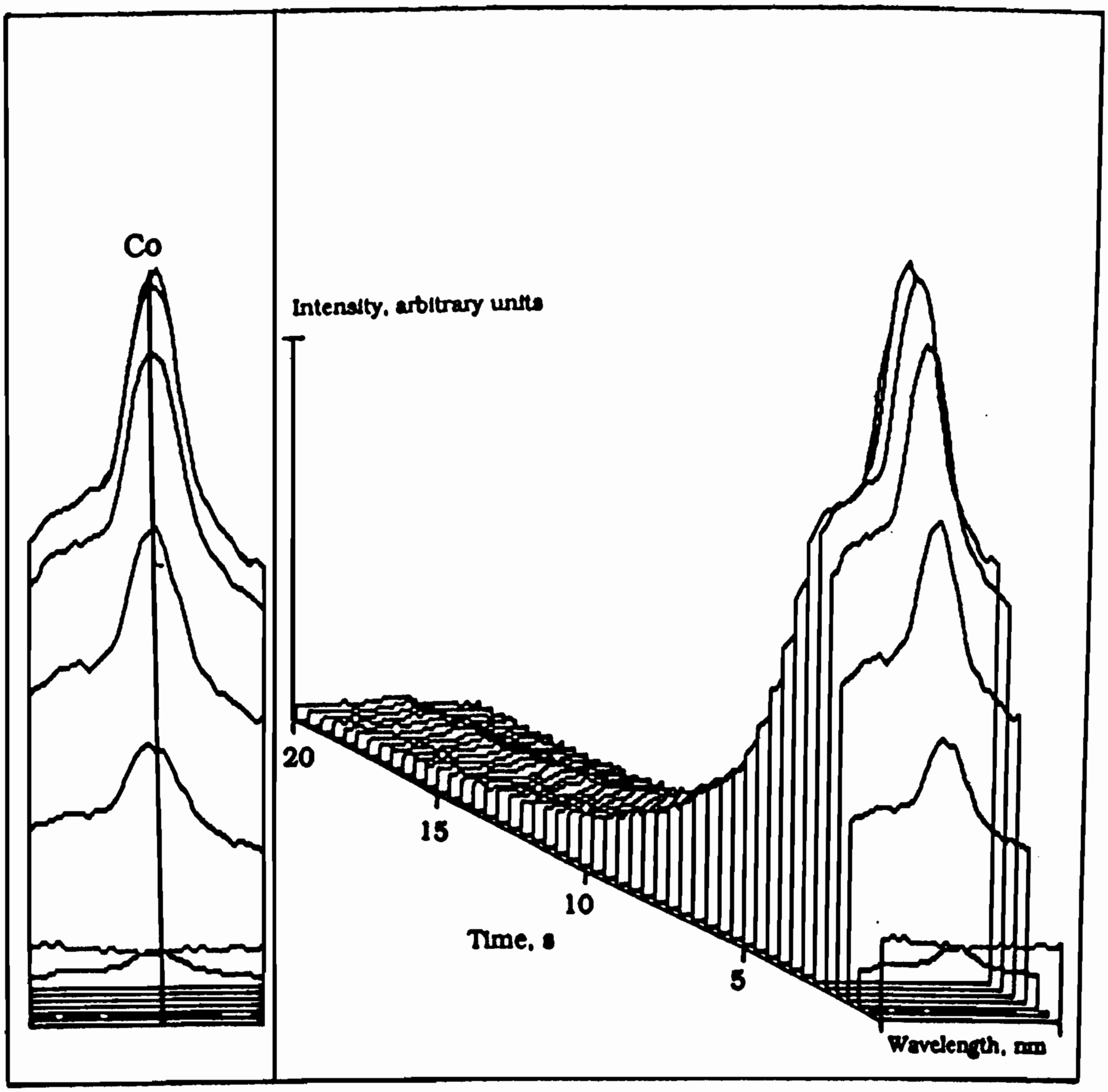


Figure 13.b)-
Signal of Co from the insertion a 125 mg pellet of 1:1:5 AgCl/PACS-1/graphite.
concentration : 17.5 ppm
wavelength span : 0.064 nm in 32 steps

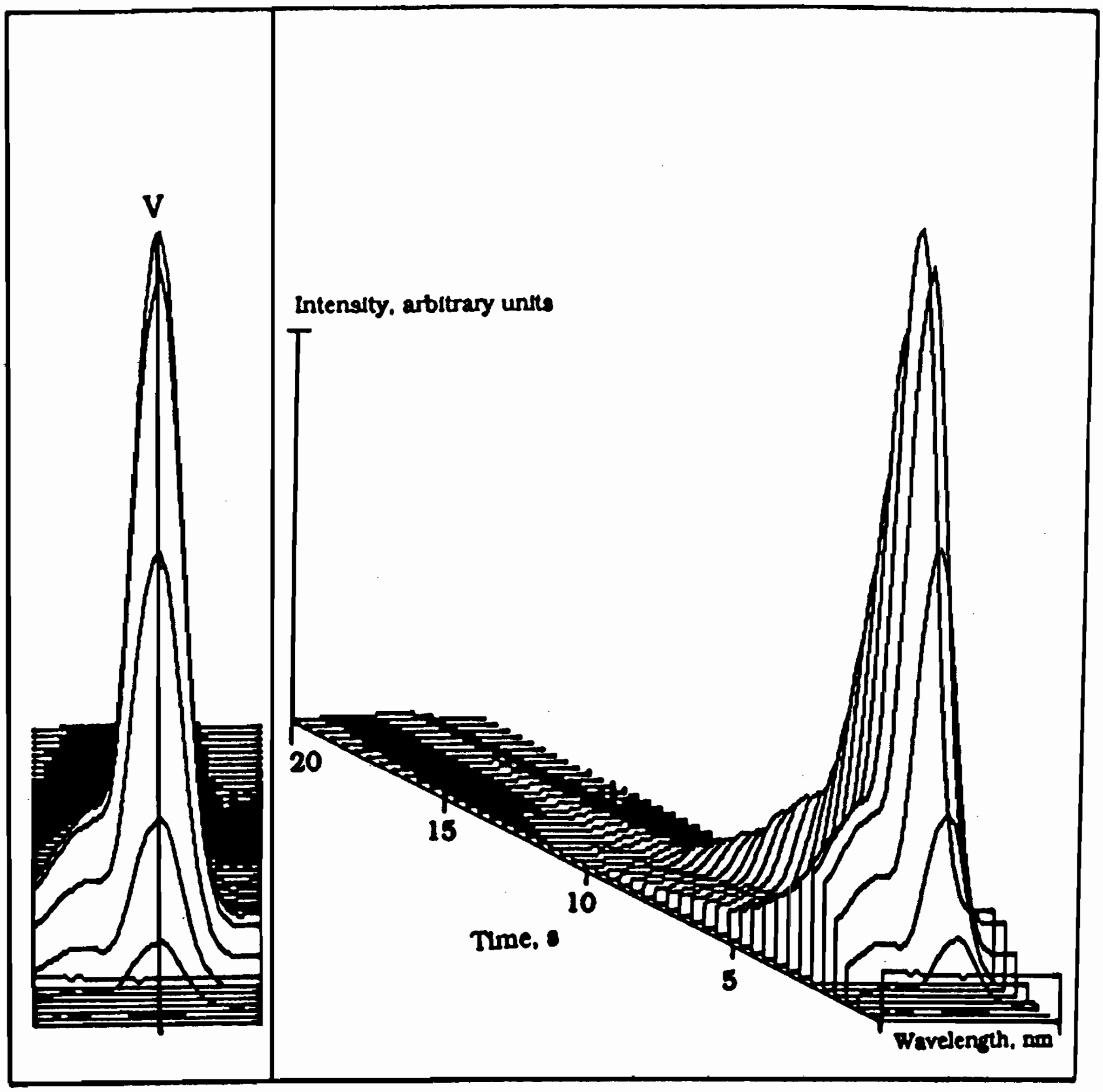


Figure 13.c)-
Signal of Cr from the insertion a 125 mg pellet of 1:1:5 AgCl/PACS-1/graphite.
concentration : 113 ppm
wavelength span : 0.064 nm in 32 steps

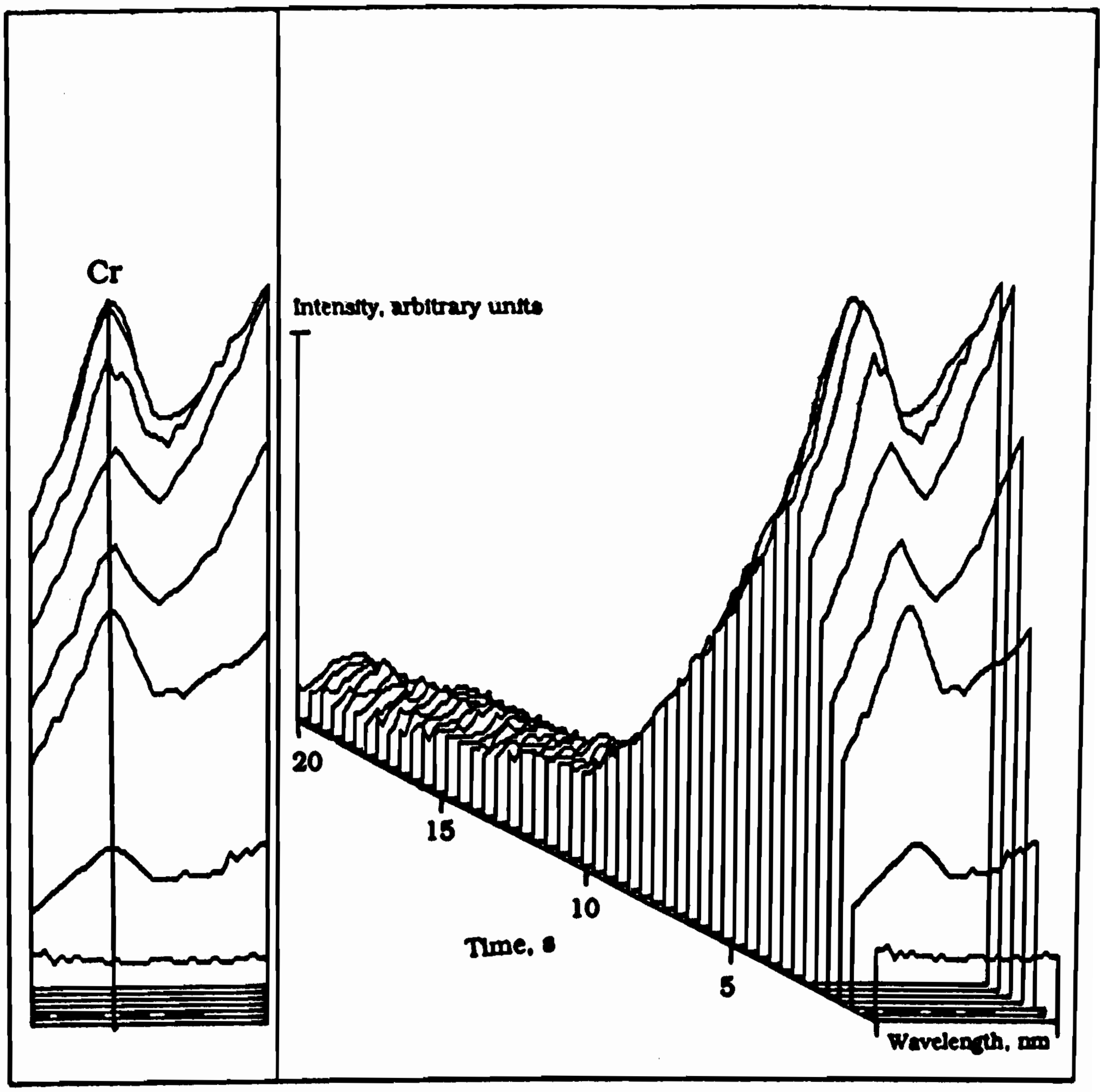


Figure 13.d)-
Signal of V from the insertion a 125 mg pellet of 1:1:5 AgCl/PACS-1/graphite.
concentration : 127 ppm
wavelength span : 0.064 nm in 32 steps

REFERENCES

1)- E.D. Salin and G. Horlick, *Anal. Chem.* **51**, 2284 (1979)

2)- D. Sommer and K. Ohls, *Frezenius Z. Anal. Chem.* **304**, 97 (1980)

3)- V. Karanassios and G. Horlick, *Spectrochim. Acta Rev.* **13**, 89 (1990)

4)- C.W. McCleod, P.A. Clarke and D.J. Mowthorpe, *Spectrochim. Acta* **41B**, 63 (1986)

5)- W.E. Pettit and G. Horlick, *Spectrochim. Acta* **41B**, 699 (1986)

6)- Y. Shao and G. Horlick, *Appl. Spectrosc.* **40**, 386 (1986)

7)- G. Zaray, J.A.C. Broekaert and F. Leis, *Spectrochim. Acta* **43B**, 241 (1988)

8)- I.B. Brenner, A. Lorber and Z. Goldbart, *Spectrochim. Acta* **42B**, 219 (1987)

9)- L. Blain and E.D. Salin, ***companion publication***

10)- R.L.A. Sing and E.D. Salin, *Anal. Chem.* **61**, 163 (1989)

11)- E.D. Salin and R.L.A. Sing, *Anal. Chem.* **56**, 2596 (1984)

12)- M.M. Habib and E.D. Salin, *Anal. Chem.* **57**, 2055 (1985)

13)- C.J. Monasterios, A.M. Jones and E.D. Salin, *Anal. Chem.* **58**, 780 (1986)

14)- L. Blain, E.D. Salin and D.W. Boomer *J. Anal. At. Spectrom.* **4**, 721 (1989)

15)- J.C. Van Loon, *Anal. Chem.* **52**, 955A (1980)

16)- V. Karanassios and G. Horlick, *Spectrochim. Acta* **44B**, 1361 (1989)

17)- P. Burgener and G. Légère, *ICP Info. Newslett.* **13**, 521 (1988)

18)- L. Blain, Doctoral dissertation, Department of Chemistry, McGill University (1991).

19)- R. Avni, A. Harel and I.B. Brenner, *Appl. Spectrosc.* **26**, 641 (1972)

20)- J.O. Burman, applications : geological in P.W.J.M. Boumans, Ed.; *Inductively Coupled Plasma Emission Spectroscopy*, Chemical Analysis series vol. 90, John Wiley and Sons, Inc: New York (1987)

21)- J.W. Olesik, spectrometers in P.W.J.M. Boumans, Ed.; *Inductively Coupled Plasma Emission Spectroscopy*, Chemical Analysis series vol. 90, John Wiley and Sons, Inc: New York (1987)

22)- G.F. Larson, V.A. Fassel, R.K. Winge and R.N. Kniseley, *Appl. Spectrosc.* **30**, 384 (1976)

23)- H. Nickel, *Spectrochim. Acta* **23B**, 323 (1968)

24)- N.W. Barnett, M.J. Cope, G.F. Kirkbright and A.A.H. Taobi, *Spectrochim. Acta* **39B**, 343 (1984)

25)- Umemoto and Kubota, *Spectrochim. Acta* **42B**, 491 (1987)

26)- V. Karanassios, G. Horlick and M. Abdullah, *Spectrochim. Acta* **45B**, 105 (1990)

27)- E.R. Prack and G.J. Bastiaans, *Anal. Chem.* **55**, 1654 (1983)

28)- A. Lorber, A. Harel, Z. Goldbart and I.B. Brenner, *Anal. Chem.* **59**, 1260 (1987)

29)- M. Abdullah, K. Fuwa and H. Haraguchi, *Spectrochim. Acta* **39B**, 1129 (1984)

30)- V. Karanassios, M. Abdullah and G. Horlick, *Spectrochim. Acta* **45B**, 119 (1990)

31)- M. Reisch, H. Nickel and M. Mazurkiewicz, *Spectrochim. Acta* **44B**, 307 (1989)

32)- J.P. Matousek and H.K.J. Powell, *Spectrochim Acta* **43B**, 1167 (1988)

33)- D.A. Skoog and D.M. West; *Fundamentals of Analytical Chemistry*; Holt, Rinehart and Winston: New York (1976), p. 613

34)- L.H. Ahrens and S.R. Taylor; *Spectrochemical Analysis*; Addison-Wesley:Reading, MA (1961)

35)- CRC Handbook of Chemistry and Physics, 66th Edition. CRC Press, Boca Raton, FL (1979)

CHAPTER 4

The feasibility of adequately recording the signal of elements of high and intermediate volatility after the insertion of pellets pressed from mixtures of sediment in graphite was demonstrated. The main objection raised by Brenner et al. remained, that the different thermal properties of synthetic standards and naturally occuring geological materials precluded the calibration of this technique.

The insertion of pellets of sediment clearly disturbed the plasma to a much greater extent than the insertion of simple standards prepared from metal oxides in graphite powder. Indeed, the effect of the insertion was such that it could be discerned by visual inspection of the plasma as the burn proceeded. Yet, there are standard methodological cures that can be applied to compensate for systematic errors, such as internal standardization and standard additions. The work done on the development of such methods for the determination of volatile elements and those of intermediate volatility has been accepted for publication as :

Methodological Solutions for the Analysis of Sediment Samples by Direct Sample Insertion Inductively Coupled Plasma Atomic Emission

Laurent Blain and Eric D. Salin
Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec H3A 2K6, Canada
SPECTROCHIMICA ACTA, PART B - TO BE PUBLISHED

Laurent Blain carried out the experimental work and the interpretation of the data, under the supervision of Prof. Salin.

ABSTRACT

Results for the calibration of the direct sample insertion technique (DSI) with sediment standards are reported for inductively coupled plasma atomic emission spectrometry (ICP-AES). It has been found that internal standardization can compensate for variations in volatilization interferences and changes in excitation conditions between sediment standards, for elements of high and intermediate volatility (Cd,Cu,Hg,Mn,Pb and Zn). It has also been found that the method of standard additions allows accurate calibration of the technique. Sub-µg/g detection limits were typical for elements of high and intermediate volatility.

INTRODUCTION

Since the early days of instrumental analyses the development of methods for the direct analysis of solids has been a subject of considerable interest. The basic motivation is economic, many hours of labour would be avoided if a technique was available that could directly handle samples in any form. With the current concern for high accuracy trace determinations, direct solid analyses are increasingly attractive, because they may also minimize contamination risks and dilutions.

The direct insertion of samples into the inductively coupled plasma (ICP) has already shown great potential with liquids [1] and is increasingly being applied to various types of solid materials [1..5]. Thanks to its exceptional performance characteristics, the ICP has rapidly established itself as perhaps the most widely used multi-element analysis technique [6]. However, sample introduction remains a weak link, and with few exceptions [7] commercial ICP instruments are practically limited to the analysis of liquids. Direct sample insertion (DSI) is one of a group of alternative sample introduction procedures that have been devised to address this weakness, along with dry powder entrainment [8], slurries [9], ablation techniques [10] and electrothermal vaporizer [11].

In a companion publication we reported recent progress in the development of instrumentation and methodologies for the direct insertion of samples of sediment in the ICP [12]. It was found that the direct insertion of pellets pressed from mixtures of sediment and graphite held in suitably modified graphite cups resulted in sharp signals for volatile elements like Cd, Cu, Hg, Mn, Pb and Zn. The use of volatilization enhancers was also investigated, and it was found that the addition of AgCl to the mixtures of sediment and graphite resulted in acceptable signals for refractory elements like Co, Cr, Fe, Ni and V.

We find that the outlook on solid analyses before we undertook the sediments project is best expressed by the opposing views of Horlick et al. [3,4] and Brenner et al. [13]. Horlick's outlook is very optimistic, based on work done with various coals, botanicals and powdered arc standards (SPEX g-standards, graphite matrix). He suggests that DSI is capable of good reproducibility, has a wide linear dynamic range, is mostly free from matrix interferences and offers superb detection limits. Brenner's appraisal, on the other hand, is very pessimistic, based on work with synthetic silicate standards and various geological samples. That report concluded that matrix interferences are abundant during volatilization, with dire consequences for the technique's calibration. The main thrust of Brenner's argument is that the analyte's volatilization is not determined by the same thermal properties in synthetic standards as in naturally occurring geological materials. However, Brenner's DSI system used side-on insertion [13] while Horlick's used the more common axial insertion [1,3,4], which hindered the direct comparison of their results [12].

This paper will report results supporting our view that DSI is a viable technique for the analysis of solids of geological origin. The main concern in this paper will be to demonstrate that the technique can be calibrated with a level of accuracy comparable to that of conventional ICP-AES analyses for elements with high and intermediate volatility. Some observations on the technique's sampling statistics will also be discussed, with a view to establishing the technique's effective limits of quantitation.

EXPERIMENTAL

The direct sample introduction device and the direct reading spectrometer used for this work have already been described in a companion publication [12]. The preparation of the pellets has also been described [14] and is only different here in that a third component was added to the mixtures from which the pellets were pressed for the standard additions experiment.

The G-standards that were used to spike the samples in the standard additions experiment come in seven steps (0.0001%, 0.00033%, 0.001%, 0.0033%, 0.01%, 0.033% and 0.1%) for every element but the internal standard (In @ 0.1%). The standard additions samples were prepared by adding a variable quantity of G-standard of appropriate concentration to the mixture of sediment (PACS-1) and briquetting graphite.

To keep the proportion of sediment matrix constant in the mixtures, the amount of graphite was adjusted for each addition of G-standard. For example, the calibration data for Cd in Figure 4-a) goes from 0 to 10 μg/g in four increments :

mixture concentration	mass of graphite (mg)	mass of G-standard (mg)	G-standard used
0 μg/g	3.000	0	
1 μg/g	2.950	0.050	0.001%
2 μg/g	2.900	0.100	0.001%
4 μg/g	2.940	0.060	0.0033%
10 μg/g	2.950	0.050	0.01%

The total weight of sample per batch was about 3.5 g, from which between fourteen and sixteen 225 mg pellets could be pressed.

It was found that adding more than 125 mg of G-standard significantly weakened the pellets, which favored the use of higher concentration G-standards. On the other hand, weighing, transferring and mixing small masses of powders are difficult even with a semi-micro balance, and a lower threshold of 50 mg of powder was adopted. This entailed a compromise in the choice of the spiking standard, and explains why the 4 μg/g spiked mixture was prepared with 33 μg/g G-standard but the 10 μg/g spiked mixture with 100 Og/g G-standard.

It is difficult to weigh out exactly 50 mg of powder, so the weight of each addition was recorded and the spiked mixture's concentration adjusted. The reproducibility of the signals was used as a check on the mixing operation and the RSD on peak area was about 7%, in line with the technique's established performance [4,14]. The higher concentrations were problematic because the maximum concentration for G-standards is 1000 μg/g, which entailed the use of large additions that resulted in weaker pellets.

A custom data analysis program was developed to handle the large amount of data necessary for calibrations. An interactive procedure was written in Pascal to locate the start, peak and end times of the transient signals from the on-line trace. The trace's first derivative was used to locate the peak's maximum. The start and end times were then found by scanning outward from the peak's maximum. The criterion for deciding when the baseline had been reached was whether the value at that point had fallen within a 68% confidence interval around the average of the next nine points in the scan's direction.

As already reported in a companion publication [12], the transient signals of the volatile elements and those of intermediate volatility could be resolved temporally from spectral interferences by a co-optimization of the system's operating parameters (especially cup geometry and plasma power). Eventually, a simple exposure with a single off-line background estimate could be used to adequately record the signals. The baseline of the on-line trace was interpolated from the off-line trace by a cubic spline over the interval from the start to the end of the peak, and subtracted point by point. Numerical integration was found to provide the best compromise between accuracy and execution time.

RESULTS AND DISCUSSION

Standardization

The three sediment reference materials (SRM) from the National Research Council of Canada (NRCC) used in this work do not differ much in terms of their bulk composition. The concentrations of matrix and minor constituents are listed in the first part of Table 1 for BCSS-1, MESS-1 and PACS-1. From an atomic spectroscopist's perspective, these matrices are virtually identical. Indeed, visual observation of the burns initially suggested that they proceeded much the same for the three SRM, and a preliminary inspection of the signals after each burn also failed to reveal any significant difference. Variations in the magnitude of the signals of trace elements between sediments were taken to reflect their different concentration profiles. The concentrations of selected trace elements in the three SRM are also compiled in Table 1.

The signals that were recorded for the volatile elements with an optimized system were well resolved from background interferences [12]. A single off-line background measurement was sufficient to permit adequate baseline subtraction at all the channels of interest, as shown in Figure 1 for Hg. Background correction and peak integration were carried out by the data analysis program written for this particular application, which was discussed in the Experimental section. Response factors were then calculated for every element studied by taking the ratio of the corresponding peak areas and concentrations.

The response factors of elements in the same volatility category were found to vary systematically between the three SRM. The average response factors of Cd, Hg, Pb and Zn in each SRM are arranged in Table 2, and it is obvious that they vary in like manner for the four elements between SRMs. The response factors were then normalized relative to those of one SRM picked arbitrarily (i.e. the response factors of the four elements in the three SRM were respectively ratioed to those in BCSS-1). A two way analysis of variance (ANOVA) was then performed on this data to determine whether the normalized response factors differed significantly across the elements and across the SRM. At least ten replicate insertions had been run for each SRM, and only one of the ten replicate insertions of BCSS-1 chosen at random was used to normalize the response factors. This provided at least nine independent data for each cell, and at the 99% confidence level only the variation between SRMs was found significant.

The signals of Cd, Hg, Pb and Zn in the three SRMs are shown in Figure 2, and visual inspection of these signals failed to reveal any obvious difference in either appearance time or shape. This was one instance where the transient nature of DSI signals held particularly useful diagnostic information. If an analyte was trapped in a refractory matrix, both the appearance time and the shape of its signal would be affected. Indeed, many reports on DSI have established volatility categories similar to those of arc spectroscopy, based on appearance time [13,15,16,17]. Furthermore, no signal was seen for these elements when the burned pellets were ground, mixed with AgCl, and inserted in the plasma again [12]. That the burns proceed identically and to completion for volatile elements in the three sediments was thus verified. Likewise, the signals of Cu and Mn did not differ noticeably between SRMs, although the ratio of their response factors differed from those of the more volatile elements. A second burn, after the addition of a volatilization enhancer confirmed that these elements of intermediate volatility are also completely vaporized during the first insertion.

The large volumes of gases generated during the early part of the burn are bound to affect the thermal excitation of analyte atoms. With conventional sample introduction systems, it is well documented that the injection of a wet aerosol into the plasma alters excitation conditions [18,19,20]. Indeed, the plasma is eventually extinguished as the amount of water introduced into the discharge is increased. The plasma's continuum emission was visibly dimmed after the insertion of the probes, and the plasma was sometimes extinguished when the ratio of sediment to graphite in the pellets was increased above 1 part in 5 [12]. It is not only likely that the temperature of the plasma was lowered, but that this drop also depended on the composition and volume of the vapors escaping from the sample. The entrainment effect of the streaming gases would also contribute to lower the efficiency of the excitation step, by shortening the analyte's residence time in the plasma.

Such physical interferences are not unique to DSI, and methodological cures for very similar problems have been devised by arc spectroscopists [21]. Internal standards come to mind first, and indeed a rare volatile element such as gallium could be added in fixed amounts to the mixtures of sediment in graphite for that purpose. Of course, just as with the arc [21], it would be essential to match carefully the physical and spectroscopic properties of the internal standard with those of the elements of interest. To show how the method of internal standards could compensate for the physical interferences at work early in the burn, one of the volatile elements was chosen as an internal standard for the other three. The integrated signals of Hg, Pb and Zn were ratioed to the response factor of Cd in each of the three SRM and plotted against their respective concentrations. The standardization curves thus obtained were linear (Figure 3), with the standard errors on their slope falling between 8 and 15%.

Apart from being difficult to choose, internal standards also have the disadvantage of requiring an additional channel each. However, the calibration of the technique is simple provided that a few suitable standard reference materials are available. In routine applications where similar samples are analyzed, the effort involved with developing a suitable internal standard mixture is worthwhile. The simplicity of external calibration, using standard reference materials spiked with the internal standard mixture, far outweighs the difficulty of choosing internal standards for the various classes of elements.

Calibration

The method of standard additions is commonly used to correct for interferences that affect the slope of the calibration curve when an adequate blank estimate (i.e. the calibrations curve's y-intercept) is available [22]. When it is difficult to duplicate the sample matrix, known additions of standards can be used to compensate for nonspectral interferences and certain types of spectral interferences which enhance or depress the analytical signal by a fixed fraction independent of analyte concentration. The basic idea is to make a "standard" out of the sample.

The standard addition procedure is often used improperly due to a failure to understand the assumptions it involves, and to avoid this mistake it is necessary to first assess how well these assumptions are met. First, there must be a good blank measurement, the baseline subtraction procedure described in the last section takes care of that. Second, the signal must be linearly proportional to analyte concentration, and the multiple addition procedure provides a check on this assumption. Third, analyte interferences must increase or decrease the analytical signal from the original analyte in the sample and the analyte added in the standard spike by the same constant fraction independent of analyte concentration. This is the hardest assumption to verify. An independent estimate of the analyte's concentration is the only way to verify that the calibration is accurate.

Powdered arc standards (SPEX G-standards, graphite based) were used to spike mixtures of PACS-1 in graphite, and the calibration curves that were obtained for trace volatile (Cd @ 2.38 μg/g, Hg @ 4.57 μg/g, Pb @ 404 μγ/γ & Zn @ 824 μg/g) and intermediate (Cu @ 452 μg/g & Mn @ 470 μg/g) elements are plotted in Figure 4. Each point is an average of the background corrected signals from five replicate runs that were integrated with the data analysis program described earlier. The relative standard deviations (RSD) of the integrated signals fell between 5 and 10 percent, which compares favorably with other methods [23]. After it was established that there were no significant deviations between the average of the sets of replicate concentration estimates and the certified values, the corresponding standard deviations were used to estimate accuracy. As seen in Table 3, the accuracy of the determination of the first three volatile elements and the two elements of intermediate volatility ranged from 4 to 8 percent, which is in line with the routine performance of the ICP with solutions sample introduction [22]. The signals of the spiked samples were different in intensity rather than shape, from the base mixture of PACS-1 in graphite. Apparently, the volatilization of these elements is not controlled by the thermal properties of the bulk matrix and their chemical form need not be carefully matched between sample and spiking standard.

The determination of elements at concentrations above 500 μg/g was not as good however, because large increments of the graphite based G-standards had to be added to the mixtures. The additions work well only with small masses of the most concentrated G-standards, because their graphite matrix is very different from briquetting graphite, and pellets made with a significant proportion of G-standards are much more fragile. This was confirmed by making up the same spikes with G-standards of different concentrations. It was found that the integrated signal was not the same when small masses of concentrated standards were used (i.e. 1/100 part of 100 µg/g) and when larger additions of less concentrated standards were used (i.e. 1 part of 1 µg/g). Furthermore, the pellets that were made up of a larger fraction of G-standards always cracked and were more likely to shatter than the others. Also, the burn was noticeably more rapid and visibly noisier with these pellets.

The determination of Zn, a volatile element at 824 µg/g in PACS-1, had noticeably poorer accuracy. A deviation close to 20% was found between the average concentration estimate obtained by standard additions and the certified value. While the concentration estimates from six determinations by standard additions had been scattered around the certified value for the other elements, the concentration estimates of zinc were systematically above the certified value (cf. Table 3). It had already been found that pellets prepared from plain G-standards were not as robust as those prepared from a mixture of G-standards in briquetting graphite. To calibrate the higher concentrations, it was necessary to add large increments of G-standards to the mixtures of sediment and briquetting graphite. The pellets prepared from these mixtures were noticeably weaker than those with smaller spikes of G-standards, and many shattered upon their insertion in the plasma. Although weaker pellets had not resulted in calibration errors for mixtures of G-standards and briquetting graphite only, the same was not true of mixtures of sediment, G-standards and briquetting graphite. Sediments release large volumes of gas early after their insertion in the plasma, and weaker pellets often cracked with the gases pulling the analyte along. The shortened residence time of the analyte in the plasma would, in turn, reduce the slope of the calibration curves. Because the signal of the unspiked sample remains the same (i.e. fixed y-intercept), a reduced slope pushes the x-intercept further in the negative direction and results in an exaggerated concentration estimate.

This problem is not intractable, but it is a compelling reason for customizing the spiking standards for the intended material. These investigations have shown that, at least for the volatile and intermediate elements, the standards need not be matrix matched to the samples. As long as the bulk composition of the pellets is not significantly affected by the spikes, precision limited accuracy can be achieved. If the spiking standards were prepared with the same pelletizing graphite that makes up the bulk of the pellets, larger spikes would not significantly weaken them. Likewise, if the concentration profile of the standards was in line with that of the samples but higher by two or three orders of magnitude, the same small additions could be used to determine all the elements of interest simultaneously.

Detection Limits

The slope of the calibration curves obtained by the method of standard additions were used to calculate DSI detection limits in PACS-1 for the six elements studied. The standard deviation of the off-line background signal integrated over the peak's duration was used to estimate blank noise. The detection limits of Table 4 were calculated as three times the ratio of blank noise to the slope of the corresponding calibration curve.

It is important to note that there is a significant degradation in the homogeneity of an analyte's distribution as its effective mass in the sample falls below a threshold [24,25], irrespective of the technique's detection limits or precision. During early characterizations of our DSI system with G-standards [12], we had observed that the RSD on peak areas deteriorated at concentrations below 1 µg/g for most elements with graphite cups. However, we had also found that with a 250 mg pellet the RSD on the average peak area for a 1 µg/g mixture of G-standard was back down to its normal level. That an increase in mass resulted in a commensurate improvement in analytical precision is an important finding, because it suggests that using larger sample loads would extend the effective operating range much closer to the estimated detection limit.

CONCLUSION

The determination of volatile elements and those of intermediate volatility in sediments by DSI-ICP-AES is feasible. The calibration of the technique is not as problematic with these matrices as had been suggested earlier by others [13]. It has been found that the matrix effects affecting the early part of the burns can be addressed with standard methodological cures, internal standards and standard additions. The limits of detection that were obtained here are high by DSI standards [1], especially where mass spectrometric detection (ICP-MS) has been used [26,27]. However, as already noted, most of the work done so far with DSI has been applied to simple materials and there were few possibilities for interferences due to matrix effects. On the other hand, such interferences abound with geological matrices [28,29,30] and others had all but dismissed DSI for these materials [13]. In this light, sub-µg/g detection limits are probably more realistic estimates of the technique's true potential for the analysis of complex samples.

The determination of refractory elements is more difficult because thermochemical reagents must be used to enhance their volatility [4,5,31,32]. In a companion publication [12], it was shown that AgCl can be used to release refractory elements like Co, Cr, Ni and V. However, the use of volatilization enhancers resulted in more violent burns and exacerbated interferences which have not yet been remedied by the methodological cures presented here.

To geologists the materials that were studied here are simple. BCSS, MESS and PACS are representative of a group of poorly consolidated sediments in which a major part of the trace elements are not strongly bound to the silicate matrix, but adsorbed on the surface of clay minerals. On the other hand, igneous and metamorphic rocks consist of high temperature silicate matrices in which refractory minerals containing the trace elements are trapped. Nonetheless, the physical and spectral interferences encountered with these sediments are illustrative of difficulties that can be expected in the analysis of many geological samples.

TABLE 1
composition of three marine sediment reference materials, BCSS-1, MESS-1 and PACS-1. Matrix and minor constituents - (percent)

	BCSS-1	MESS-1	PACS-1
Al_2O_3	11.83	11.03	12.23
C	2.19	2.99	3.69
CaO	0.760	0.674	2.92
Cl	1.12	0.82	2.39
Fe_2O_3	4.70	4.36	6.96
K_2O	2.17	2.24	1.50
MgO	2.44	1.44	2.41
Na_2O	2.72	2.50	4.40
P_2O_5	0.154	0.146	0.233
S	0.36	0.72	1.32
SiO_2	66.1	67.5	55.7
TiO_2	0.734	0.905	0.703

selected trace elements of high and intermediate volatility - (µg/g)

	BCSS-1	MESS-1	PACS-1
Cd	0.25	0.59	2.38
Cu	18.5	25.1	452
Hg	0.129	0.171	4.57
Pb	22.7	34.0	404
Mn	229	513	470
Zn	119	191	824

TABLE 2
comparison of response factors of volatile elements in three marine sediment reference materials, BCSS-1, MESS-1 and PACS-1

Element	SRM	A_{peak}[1] (counts[2])	R[3] (counts/µg/g)
Cd	BCSS-1	456×10^3	1825×10^3
	MESS-1	377×10^3	639×10^3
	PACS-1	1059×10^3	445×10^3
		$R_{BCSS\text{-}1}/R_{PACS\text{-}1}$	: 4.10
		$R_{BCSS\text{-}1}/R_{MESS\text{-}1}$	: 2.86
		$R_{MESS\text{-}1}/R_{PACS\text{-}1}$	: 1.44
Hg	BCSS-1	959×10^3	7437×10^3
	MESS-1	441×10^3	2580×10^3
	PACS-1	8302×10^3	1816×10^3
		$R_{BCSS\text{-}1}/R_{PACS\text{-}1}$	: 4.09
		$R_{BCSS\text{-}1}/R_{MESS\text{-}1}$	: 2.88
		$R_{MESS\text{-}1}/R_{PACS\text{-}1}$	: 1.42
Pb	BCSS-1	491×10^3	21.6×10^3
	MESS-1	262×10^3	7.72×10^3
	PACS-1	2143×10^3	5.31×10^3
		$R_{BCSS\text{-}1}/R_{PACS\text{-}1}$	: 4.08
		$R_{BCSS\text{-}1}/R_{MESS\text{-}1}$	: 2.80
		$R_{MESS\text{-}1}/R_{PACS\text{-}1}$	: 1.46
Zn	BCSS-1	487×10^3	4.09×10^3
	MESS-1	270×10^3	1.41×10^3
	PACS-1	827×10^3	1.00×10^3
		$R_{BCSS\text{-}1}/R_{PACS\text{-}1}$	: 4.08
		$R_{BCSS\text{-}1}/R_{MESS\text{-}1}$	: 2.90
		$R_{MESS\text{-}1}/R_{PACS\text{-}1}$	: 1.41

1)- A_{peak} is the average integrated peak area, corrected for slight differences in the ratio of sediment to graphite between batches (nominal - 1:5) and variations in the weight of the pellets (average - 125 mg)

2)- counts are an arbitrary unit commonly used in atomic emission spectrometry with integrating detectors such as direct readers.

3)- R is a response factor calculated by taking the ratio of A_{peak}, in counts, and analyte concentrations in µg/g

TABLE 3
replicate concentration estimates (in µg/g) determined by the method of standard additions for six trace elements in PACS-1(1)

	Cd	Cu	Hg	Mn	Pb	Zn
	2.23	467	4.74	496	394	1038
	2.44	438	4.25	476	426	943
	2.69	479	4.32	423	438	1057
	2.37	405	4.89	506	381	927
	2.35	497	4.66	489	385	876
	2.24	423	4.55	419	415	1014
average	2.39	452	4.57	468	406	976
%RSD	7	7	5	7	5	7
error(2)	0.4%	0.0%	0.0%	- 0.4%	0.5%	18 %

(1)- spiking standard : SPEX g-standards
(2)- error : $(C_{average} - C_{reference}) / C_{reference}$

TABLE 4
pellet DSI detection limits for six elements in a 1:5 mixture of PACS-1 in graphite

Element	Detection limit (µg/g)
Cd	0.01
Cu	8
Hg	0.01
Mn	0.3
Pb	0.07
Zn	0.02

(1)- detection limits corrected for 1:5 dilution PACS-1/graphite
(2)- average weight of pellets : 125 mg

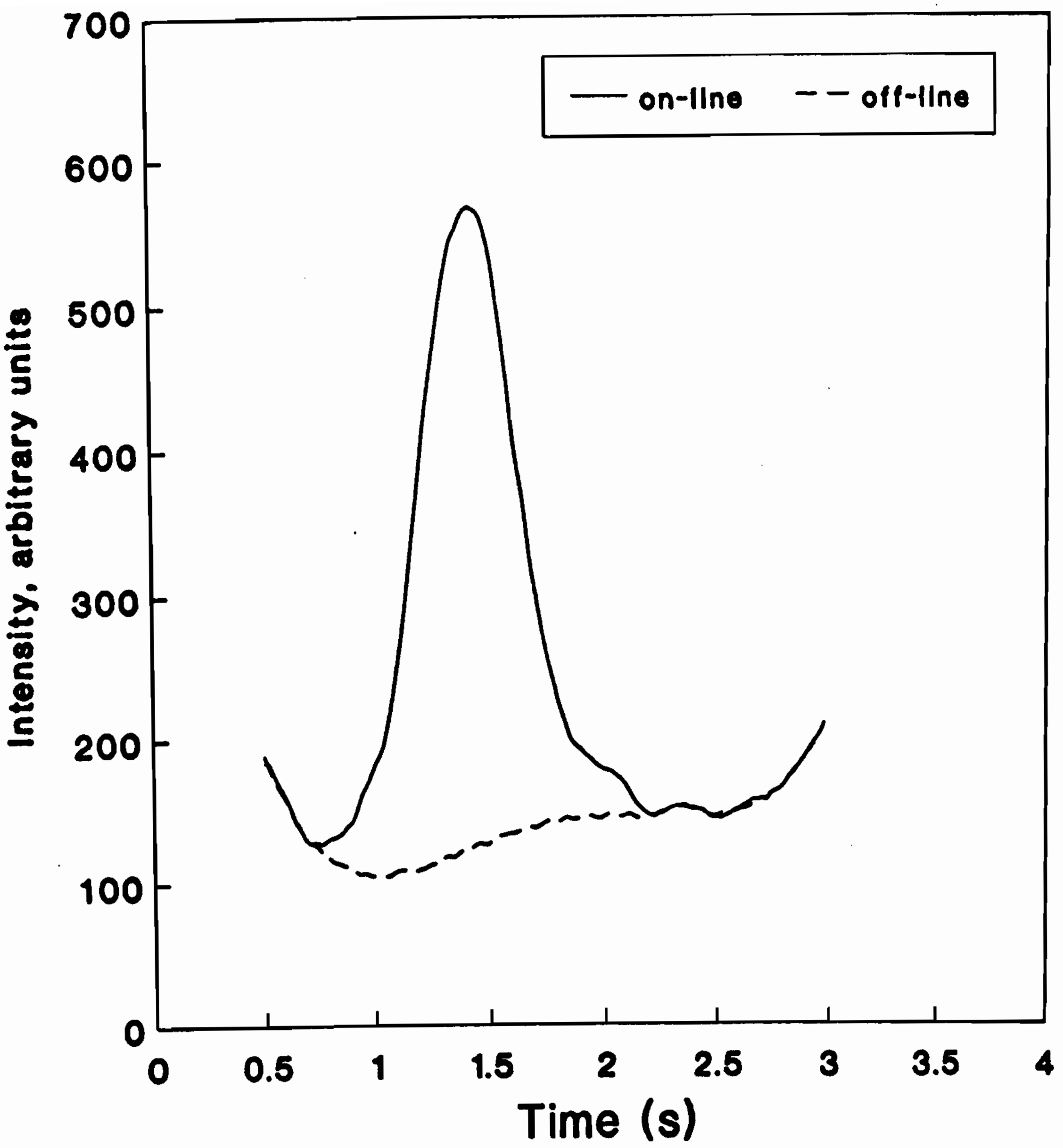


Figure 1

Signal recorded at the 253.652 nm channel of Hg for a 125 mg pellet of 1:5 PACS-1 in graphite, after the multivariate optimization of DSI and ICP parameters. A single off-line background measurement is sufficient to permit adequate baseline subtraction.

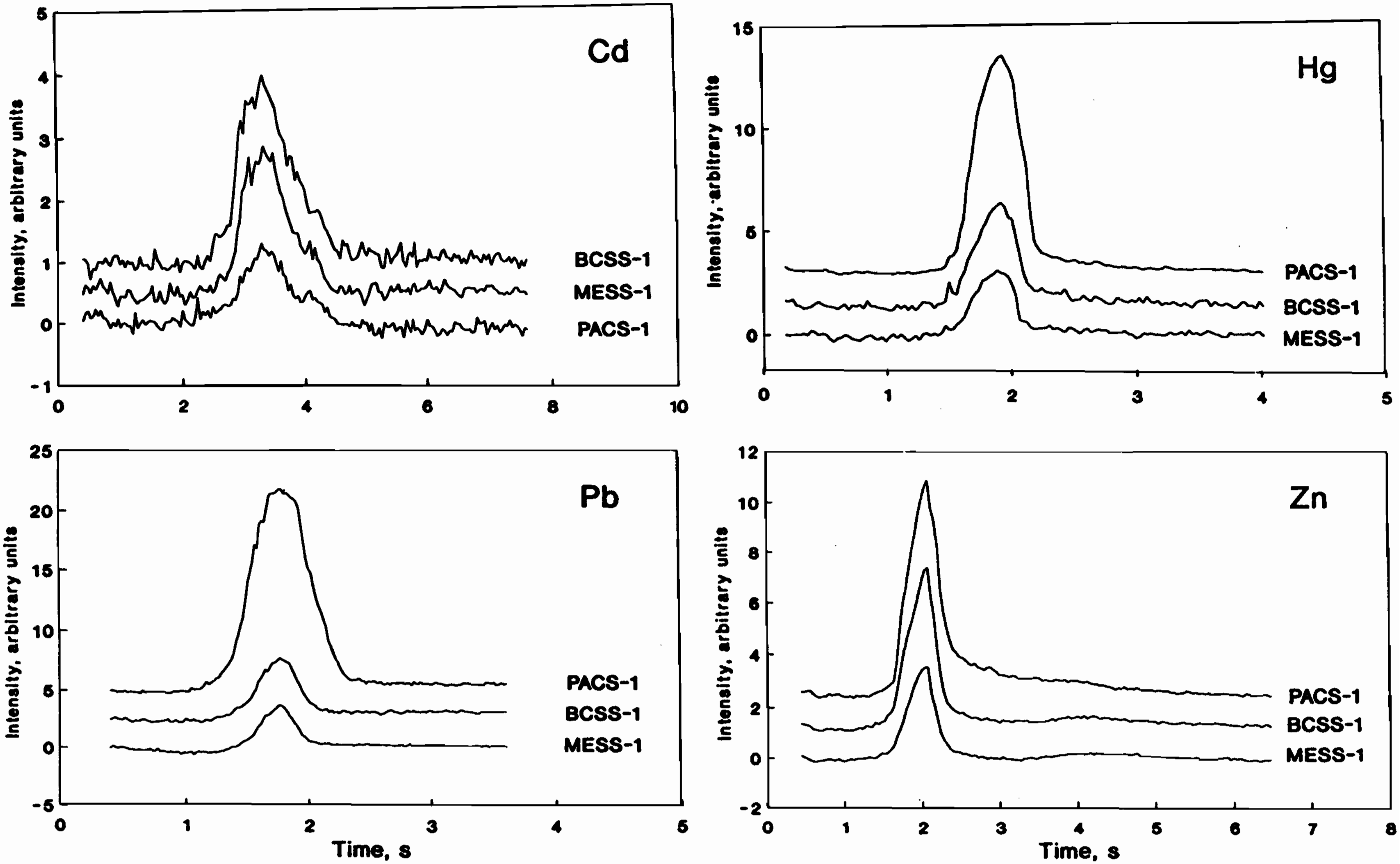


Figure 2

The signals of four volatile elements (Cd, Hg, Pb & Zn) in three sediment reference materials (BCSS-1, MESS-1 & PACS-1). Visual inspection of these signals fails to reveal any obvious difference in either their appearance time or shape between sediments.

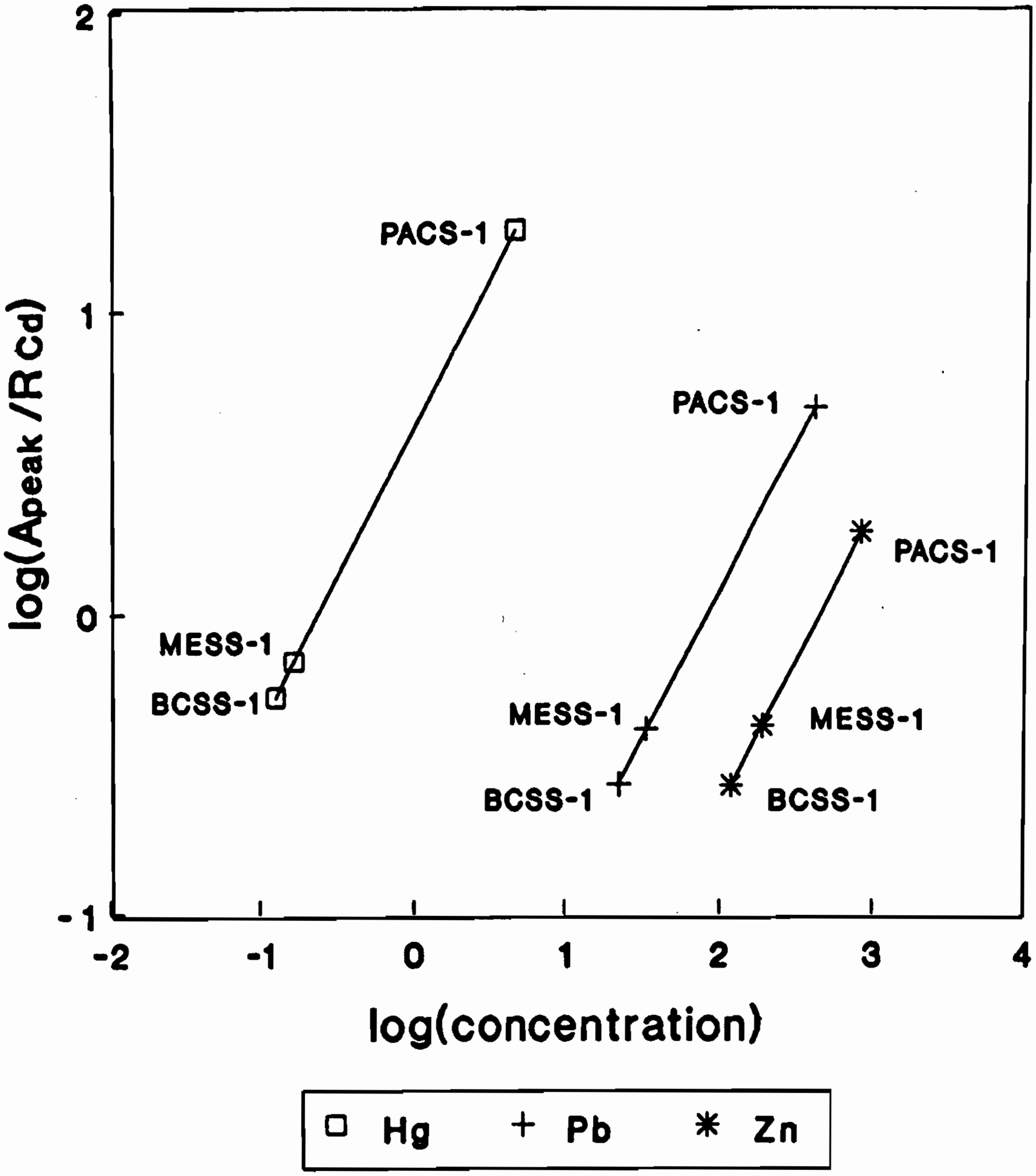


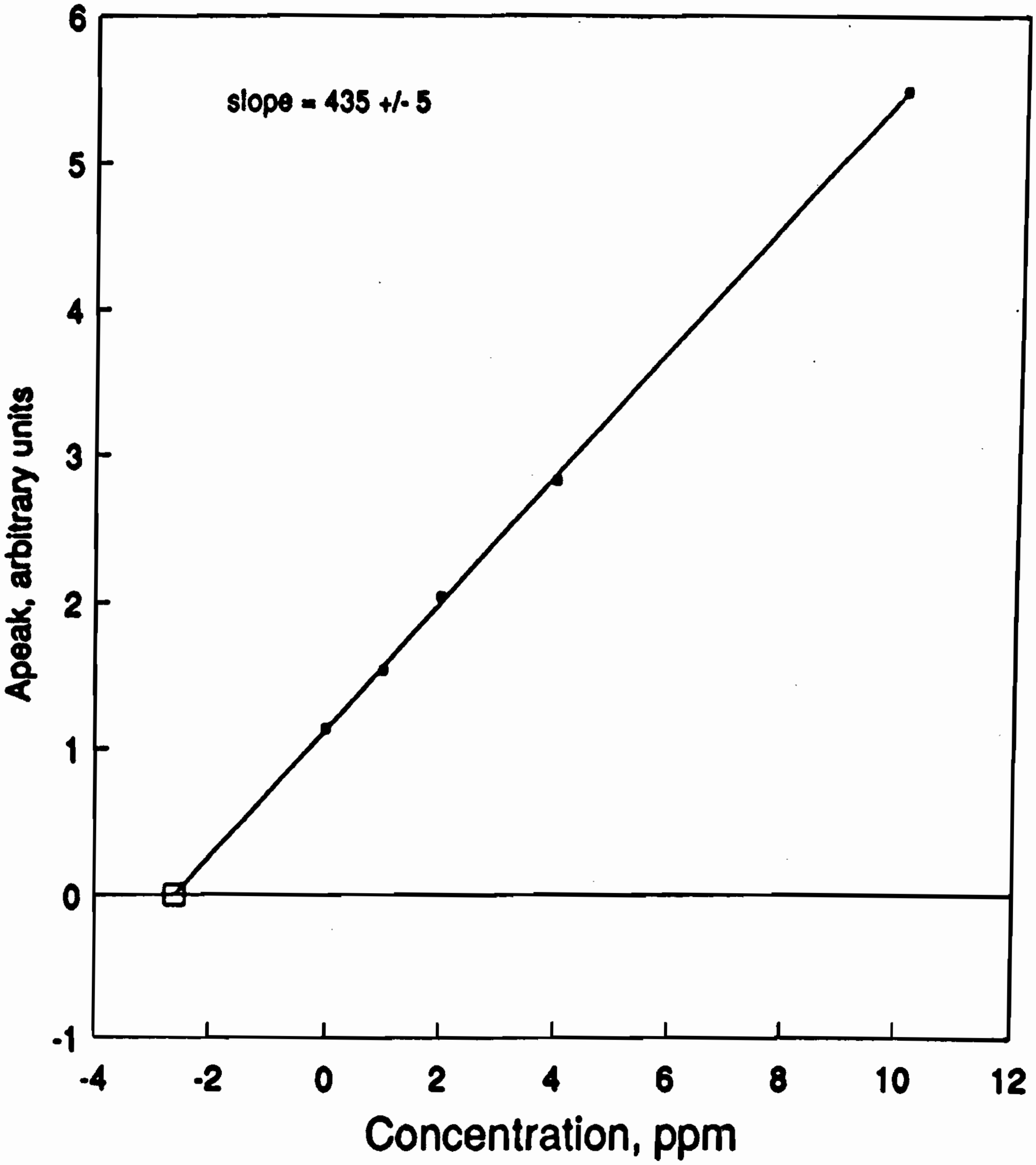
Figure 3

Log-log plot of the ratio of the integrated signals of three volatile elements (Hg, Pb and Zn) to the response factor of Cd (A_{peak}/R_{Cd}) as a function of their concentration in three sediment reference materials (BCSS-1, MESS-1 and PACS-1). Linearity of the standardization curves was confirmed by the unity slope of the log-log plots, within a 0.1 % error margin. Standard errors on the slopes of the standardization curves fell between 8 and 15 %.

Figure 4

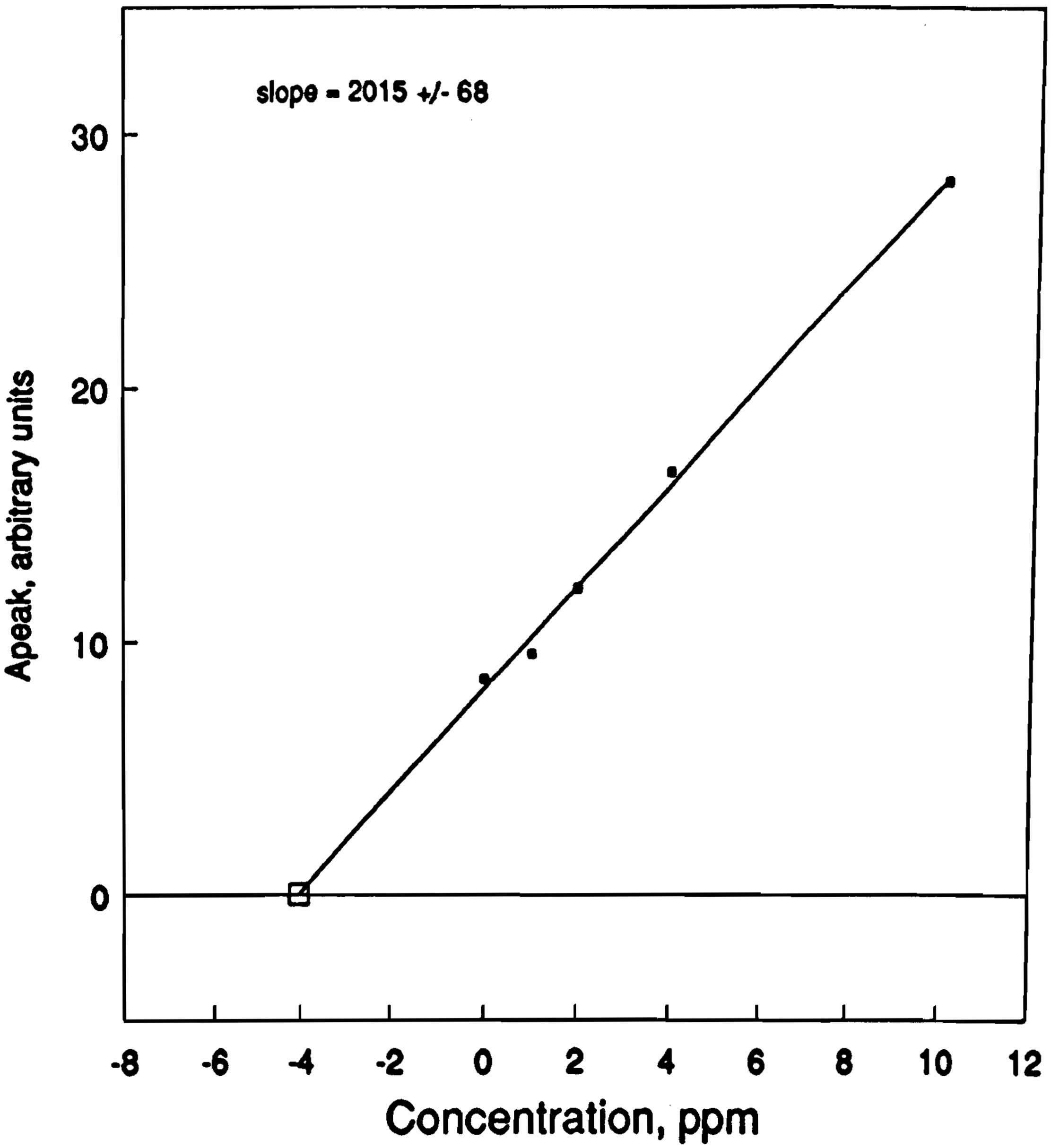
Calibration curves obtained by the method of standard additions for six elements in PACS-1

i)- volatile elements

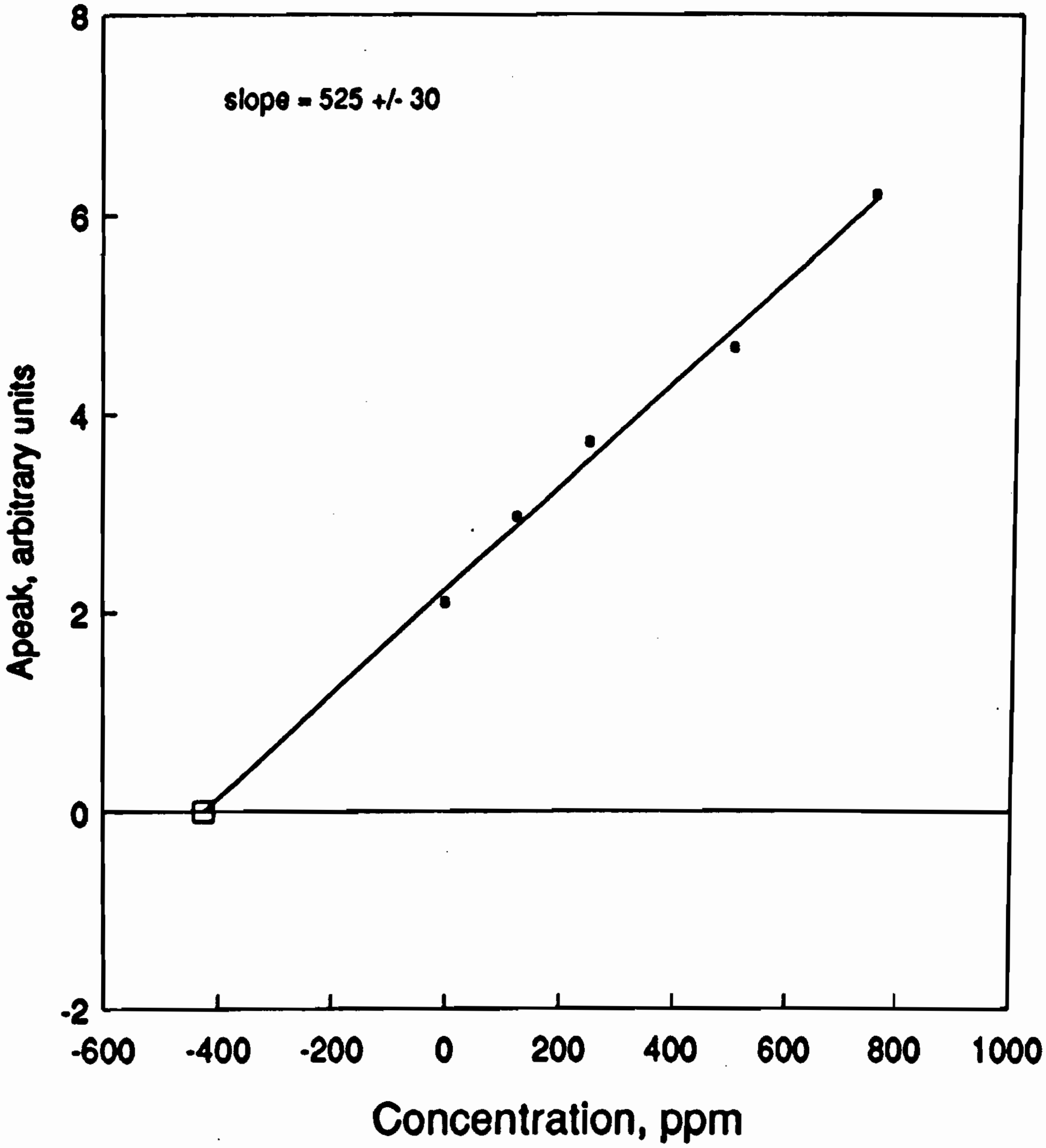


a)- Cd @ 2.38 ppm

spiking standard : SPEX g-standards

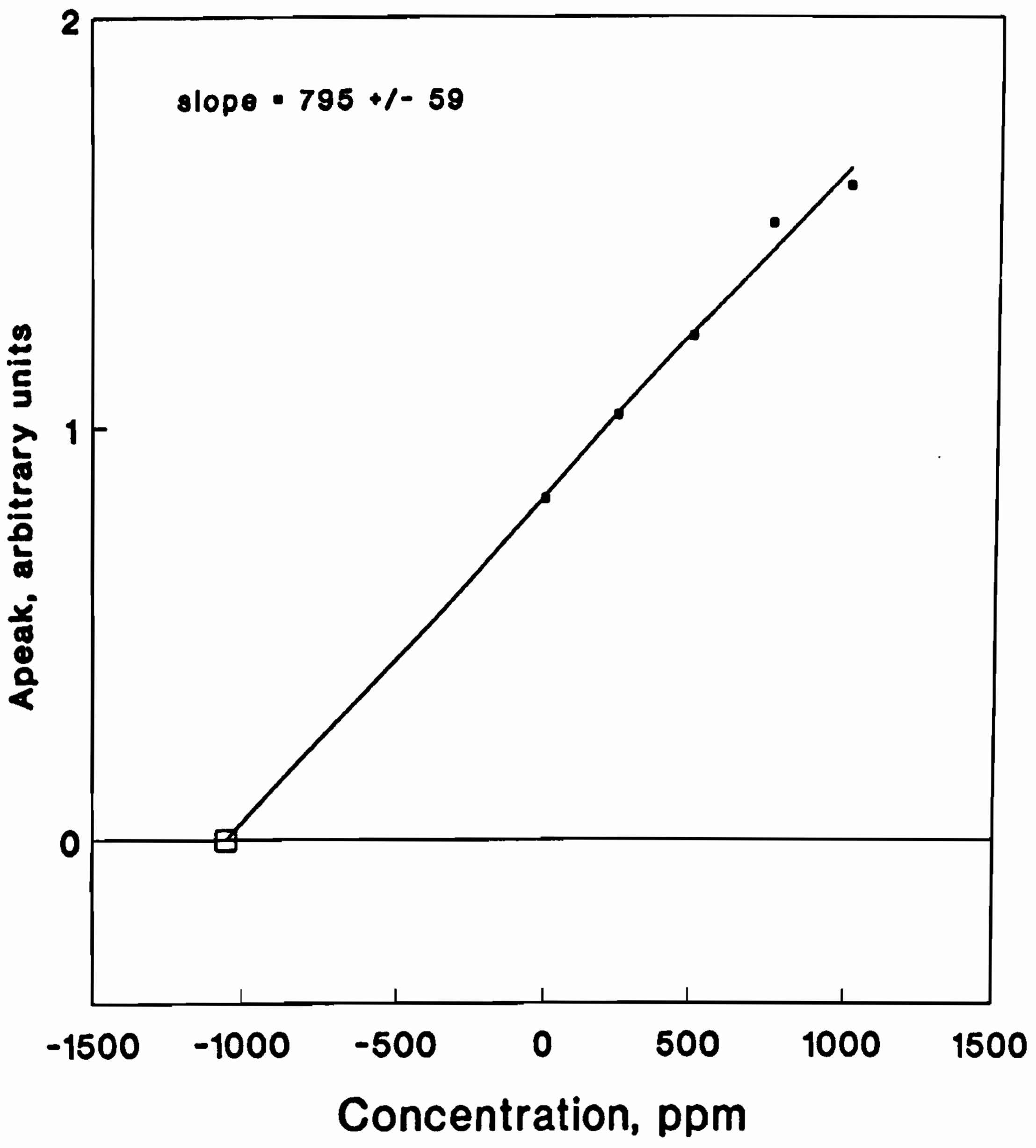


b)- Hg @ 4.57 ppm
spiking standard : SPEX g-standards



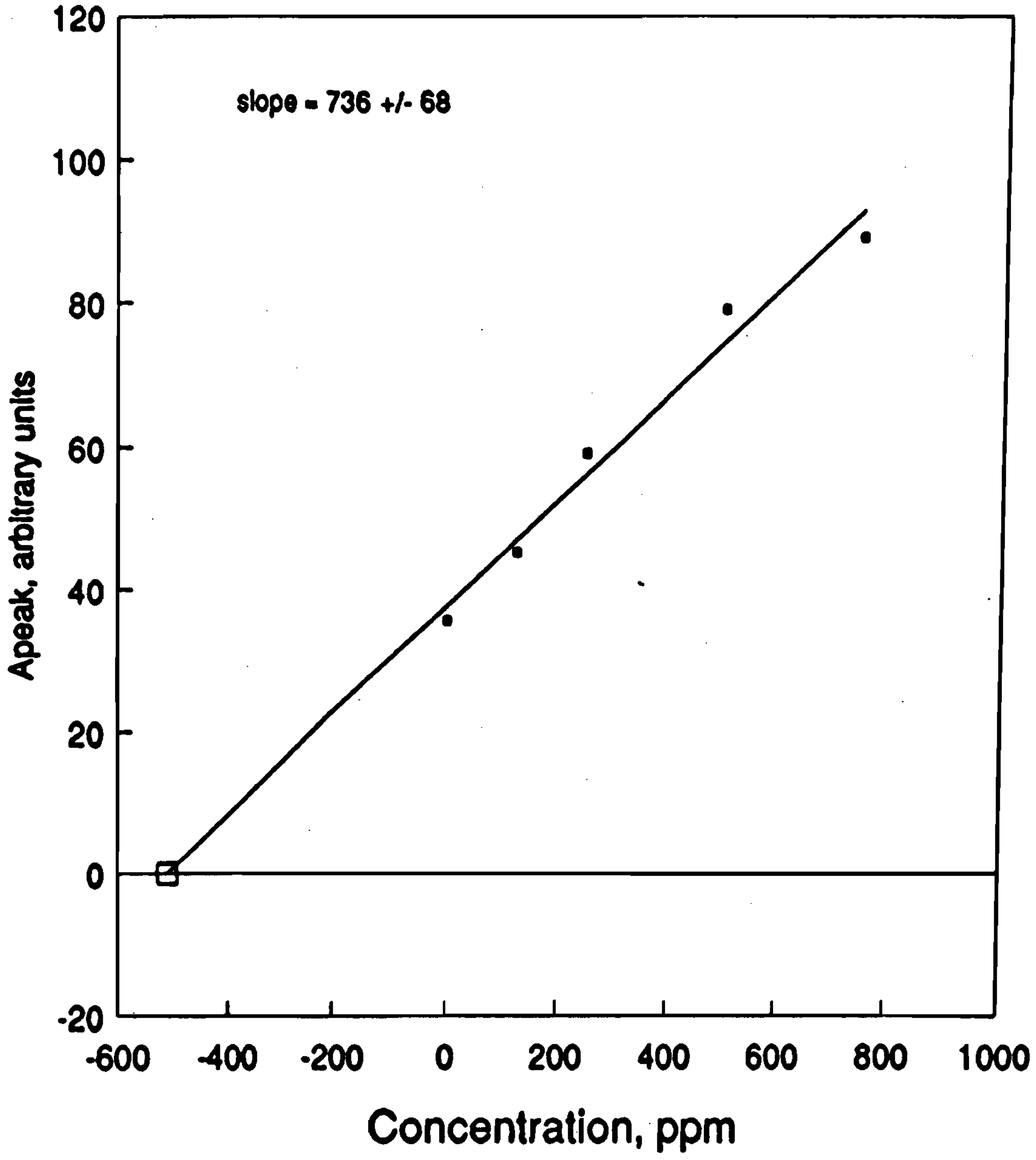
c)- Pb @ 404 ppm

spiking standard : SPEX g-standards

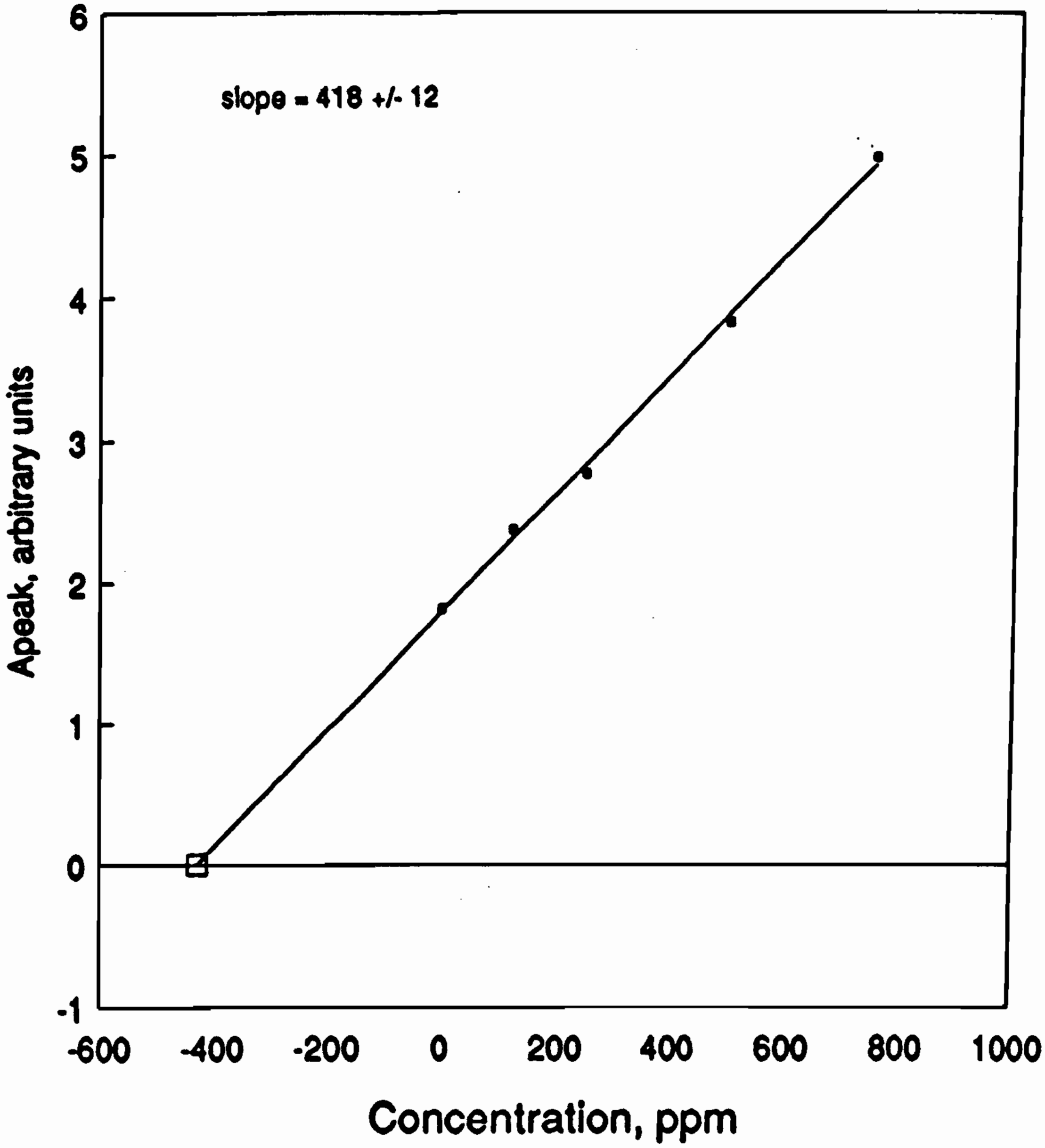


d)- Zn @ 824 ppm
spiking standard : SPEX g-standards

ii)- elements of intermediate volatility



e)- Cu @ 452 ppm
spiking standard : SPEX g-standards



f)- Mn @ 470 ppm
spiking standard : SPEX g-standards

REFERENCES

1)- V. Karanassios and G. Horlick, *Spectrochim. Acta Rev.* **13**, 89 (1990)

2)- C.W. McCleod, P.A. Clarke and D.J. Mowthorpe, *Spectrochim. Acta* **41B**, 63 (1986)

3)- W.E. Pettit and G. Horlick, *Spectrochim. Acta* **41B**, 699 (1986)

4)- Y. Shao and G. Horlick, *Appl. Spectrosc.* **40**, 386 (1986)

5)- G. Zaray, J.A.C. Broekaert and F. Leis, *Spectrochim. Acta* **43B**, 241 (1988)

6)- P.W.J.M. Boumans, introduction to atomic emission spectrometry in P.W.J.M. Boumans, Ed.; *Inductively Coupled Plasma Emission Spectroscopy*, Chemical Analysis series vol. 90, John Wiley and Sons, Inc: New York (1987)

7)- J.Y. Marks, D.E. Formwalt and R.E. Yungk, *Spectrochim. Acta* **38B**, 107 (1983)

8)- R. Guevremont and K.N. De Silva, *Spectrochim. Acta* **46B**, 67 (1991)

9)- L. Ebdon and J.R. Wilkinson, *J. Anal. Atom. Spectrom.* **5**, 67 (1990)

10)- N. Imai, *Anal. Chim. Acta* **235**, 381 (1990)

11)- W. Shen, J.A. Caruso, F.L. Fricke and R.D. Satzger, *J. Anal. Atom. Spectrom.* **5**, 451 (1990)

12)- L. Blain and E.D. Salin, ***companion publication***

13)- I.B. Brenner, A. Lorber and Z. Goldbart, *Spectrochim. Acta* 42B, 219 (1987)

14)- L. Blain, E.D. Salin and D.W. Boomer *J. Anal. At. Spectrom.* **4**, 721 (1989)

15)- V. Karanassios, G. Horlick and M. Abdullah, *Spectrochim. Acta* **45B**, 105 (1990)

16)- R.L.A. Sing and E.D. Salin, *Anal. Chem.* **61**, 163 (1989)

17)- P.W.J.M. Boumans and F.J.M.J. Maessen, *Spectrochim. Acta* **24B**, 585 (1969)

18)- M.W. Blades and B.L. Caughlin, *Spectrochim. Acta* **40B**, 579 (1985)

19)- S.E. Long and R.F. Browner, *Spectrochim. Acta* **43B**, 1461 (1988)

20)- S. Nowak, J.A.M. van der Mullen, A.C.A.P. van Lammeren and D.C. Schram, *Spectrochim. Acta* **44B**, 411 (1989)

21)- L.H. Ahrens and S.R. Taylor; *Spectrochemical Analysis*; Addison-Wesley:Reading, MA (1961)

22)- J.D. Ingle and S.R. Crouch; *Spectrochemical Analysis*; Prentice Hall, inc.:Englewood Cliffs, NJ (1988)

23)- C.G. Milward and P.D. Kluckner, *J. Anal. Atom. Spectrom.* **4**, 709 (1989)

24)- A.D. Wilson, *Analyst* **89**, 18 (1964)

25)- B. Kratochvil and J.K. Taylor, *Anal. Chem.* **53**, 925A (1981)

26)- 34)- V. Karanassios and G. Horlick, *Spectrochim. Acta* **44B**, 1345 (1989)

27)- D.W. Boomer, M. Powell, R.L.A. Sing and E.D. Salin, *Anal. Chem.* **58**, 975 (1986)

28)- J.O. Burman, applications : geological in P.W.J.M. Boumans, Ed.; *Inductively Coupled Plasma Emission Spectroscopy*, Chemical Analysis series vol. 90, John Wiley and Sons, Inc: New York (1987)

29)- I.B. Brenner, A.E. Watson, G.M. Russel and M. Concalves, *Chem. Geol.* **28**, 321 (1980)

30)- J.N. Walsh and R.A. Howie, *Mineral Mag.* **43**, 967 (1980)

31)- V. Karanassios, M. Abdullah and G. Horlick, *Spectrochim. Acta* **45B**, 119 (1990)

32)- M. Reisch, H. Nickel and M. Mazurkiewicz, *Spectrochim. Acta* **44B**, 307 (1989)

CHAPTER 5

The addition of AgCl to mixtures of sediment in graphite have been found to enhance the release of refractory elements such as Co and Cr from sediment matrices. However, the insertion of pellets prepared from mixtures of AgCl, sediment and graphite have also been found to disturb the plasma to a much greater extent than simple mixtures of sediment and graphite. To a first examination, it appeared that the methodological cures devised for the determination of volatile elements would not hold when volatilization enhancers were employed.

Further work indicated that a careful optimization of DSI and ICP parameters permitted the succesful determination of trace levels of refractory elements by the method of standard additions. The technique is demanding and requires considerable operator skill, particularly in the development stage, which may hamper its implementation as a routine method. This work has been submitted for publication as :

Application of AgCl as a Thermochemical Additive for the Determination of Refractory Elements in Sediment Samples by Direct Sample Insertion Inductively Coupled Plasma Atomic Emission Spectrometry

Laurent Blain and Eric D. Salin
Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal,
Quebec H3A 2K6, Canada
SPECTROCHIMICA ACTA, PART B - SUBMITTED

Laurent Blain carried out the experimental work and the interpretation of the data, under the supervision of Prof. Salin.

ABSTRACT

Trace levels of refractory elements have been determined in a sediment reference material (PACS-1) by direct insertion into an inductively coupled plasma (DSI-ICP-AES), using AgCl as a volatilization enhancing thermochemical additive. The method of standard additions was used for calibration. It was found that powdered metal oxide standards (SPEX g-standards) were adequate spiking standards for Co, Cr, Ni and V in PACS-1. The reproducibility of the measurements was between 10 and 25 %RSD. The accuracy of the determinations is fair below 50 µg/g, with typical errors falling below 10%, but it degrades at the higher concentrations to errors of approximately 20%.

INTRODUCTION

The direct insertion of samples into the inductively coupled plasma (DSI-ICP-AES) has already shown great promise for the analysis of solids [1-6]. The reports published so far have focused primarily on establishing performance characteristics [1-4] and have been restricted to simple matrices. Typically, volatile elements could be determined at levels down to a few parts per billion (ng/g) and matrix effects were negligible.

Two recent publications from our laboratory reported the application of DSI to the analysis of sediment reference materials [5,6], a more challenging sample type [7]. When internal standards and standard additions were employed, it was found that volatile elements could be determined with acceptable accuracy (7-15%) [6].

A major criticism leveled against DSI is that it is too restricted in the range of elements it can handle. Broadly speaking, there are three categories of elements that cannot be readily determined by DSI-ICP-AES in most matrices : (1) the carbide formers (e.g. Mo & Zr), (2) metals with a high boiling point (e.g. Ni & Co) and (3) elements present as refractory compounds (e.g. Cr_2O_3 & Al_2O_3). However, it has already been reported that thermochemical additives could be used advantageously to promote the release of these elements [3,8,9].

Thermochemical additives are usually fluorinating or chlorinating reagents that combine with refractory elements to form volatile compounds. Table 1 lists the boiling points of selected refractory elements, their carbides, oxides, chlorides and fluorides. Two early reports by Page et al. [10, 11] described a modification of the classical d.c. arc carrier distillation method to DSI-ICP-AES, using AgCl as the matrix modifier. Shao and Horlick [3] reported considerable enhancements in sensitivity for some carbide forming elements using NaF as the volatilization enhancing reagent. There was also one interesting application where Freon was used as a plasma additive [12]. Later reports [8,9,13] have compared the effectiveness of four fluoride and six chloride salts as volatilization enhancers on the basis of increased line intensities. In addition to measurements by AES, a radioactive nuclide, ^{59}Fe, has been used to determine vaporization rates for this element [9].

Because of their focus, these investigations all dealt with simple matrices, mostly graphite [3] but also α-Al_2O_3 [8]. Both of these materials have a high boiling point (Al2O3 : 2980^{o}C, graphite : ^{s}3652^{o}C) and are thermochemically inert, so they do not participate significantly in the vaporization chemistries as the burn proceeds. However, when thermochemical additives were mixed with sediments it was found that fluorinating reagents not only acted as volatilization enhancers, but also hastened the decomposition of the sediment's silicate matrix [5]. This, in turn, resulted in exacerbated physical and spectral interferences that drowned out the signals of all but the major elements.

Of the chloride salts that were tried, AgCl, $BaCl_2$, $CuCl_2$ and NH_4Cl, only AgCl resulted in significant volatilization enhancement for the refractory elements of interest (Al, Co, Cr, Fe, Ni and V) [5]. Although the burns were much smoother with AgCl than with NaF, visual observation of the plasma established that spectral and physical interferences remained a problem. Earlier, it was concluded that these interferences were not amenable to the usual methodological cures [6]. This paper will report further work that establishes the analytical potential of this technique for the determination of refractory elements in geological matrices.

EXPERIMENTAL

DSI probe

The DSI probes consist of undercut graphite cups which serve to carry pelletized powder samples into the plasma's core. In earlier studies, it was found that the geometry of the graphite cups can be used to control the flow of sample vapors through the plasma, and to improve the quality of analyte signals [5]. Figure 1 is a schematic representation of the DSI probes used for this work, the dimensions of the cups have been optimized for analyses using volatilization enhancers, as reported in the next section.

Instrument

The instrument used for this work has already been described in earlier publications [5,14]. Briefly, the direct sample insertion device is stepper-motor driven and completely under microcomputer control. The spectrometer is a modified Jarrell Ash ATOMCOMP 90750 direct reader marketed by Technical Service Laboratories [15], in which the channel cards have been upgraded and the controller has been replaced by an IBM PC compatible interface.

The salient features of the direct reader are that it is fitted with a spectrum shifter that permits partial wavelength scans, that the new channel cards are faster, and that the source code of the controller's program can be edited. The latter permits the development of custom exposures not offered by commercial instruments, such as the sequential partial wavelength scans of Figure 2.

Sample preparation

Details on the powders used for these studies are provided in Table 2. The preparation of the pellets has been described elsewhere [5,6,16], with a detailed description of the standard additions procedure [6]. The only deviation from the published standard additions procedure was the addition of AgCl to every batch of powder. A 1:1 of proportion AgCl/sediment was used because it constituted the simplest compromise between enhancing the signals of all the trace elements of interest and minimizing the spectral and physical interferences from Ag [5].

RESULTS AND DISCUSSION

Optimizations

One-shot insertions of pellets prepared from mixtures of AgCl, PACS-1 and graphite systematically extinguished the plasma. In the first second after the insertion of the probe, a very bright flash of green silver emission overtook most of the plasma. The core of the green flare was bright yellow, almost white, and the visual effect was very much like lighting a match in the middle of the plasma. The plasma was obviously disturbed as it was pushed away from the probe, and out of the load coil. The plasma was eventually blown out. Often it spontaneously relighted and was blown out again several times. It was not possible to arrive at a suitable combination of insertion speed and depth that permitted the one-shot insertion of these samples. An in-situ pre-heat under the base of the plasma was essential to condition the pellets adequately for their insertion into the plasma [5].

When the probe was brought close to its base, the plasma constricted and glowed more brightly. This is typical of in-situ pre-treatments where gases are released from the probe, such as when liquid samples are dried under the plasma [14]. When the plasma settled back down, a green glow appeared around its base and the pellet was ready for insertion. As soon as the pellet was inserted, a central channel of bright green light was formed through the plasma. After about 2 minutes, the green flare died out and was replaced by orange silicon emission.

The analyte plume was well contained in a central channel through the lower part of the plasma, but it rapidly flared out above the top of the load coil. These pellets had to be inserted higher into the plasma than pellets pressed from unmodified sediment, or some faint green light was observed around the periphery of the fireball. These observations guided the optimization of insertion depth and viewing height.

The outer dimensions of the graphite cups had already been optimized [5], and there was no obvious reason to suggest that they should be changed. It had also been found that the shallowest insertion that permitted the plasma to anchor around the cup's base worked best. The probes were therefore inserted deeply enough into the plasma's core to keep the escaping vapors contained, and the visible image of the plasma on the entrance slit's plane was used to set the viewing height. The optimal viewing height was chosen as a compromise between brighter background emission close to the fireball and turbulence higher in the plasma. This choice was justified by the earlier finding with unmodified sediments that the physical interference of gases rushing out of the probe set the optimal viewing height [5], rather than the analyte's spectrochemical characteristics.

The position and duration of the in-situ pre-heat were optimized next, and it was found that longer pre-heats with the top of the probe further away from the base of the plasma resulted in sharper peaks for the refractory elements. It had previously been determined that such pre-heats resulted in the loss of volatile elements such as As, Cd, Hg and Pb [5]. The pre-heat's conditions were adjusted with the goal of minimizing these volatility losses. The outcome was a set of compromise conditions that not only resulted in poorer signals for the refractory elements, but also in signals for the volatile elements that were not appropriate for quantitative applications. Complicating factors were chiefly the persistence of these losses, as well as worsened physical and spectral interferences. Whereas with unmodified sediments it had been possible to resolve temporally the signals of volatile elements from major spectral interferences (e.g. Fe and Si), the addition of a volatilization enhancer meant that almost everything left the cup at the same time. For example, the signals of Cd, Hg and Pb were all but buried by neighboring lines (within 0.04 nm) of Fe (@ 5% in PACS-1). At this point, it was decided that the compromise was unworkable and that a full analysis would have to be done in two steps.

The walls of the cups had been used as heat sinks to slow down the progress of the burn in previous applications, and the same was tried here. The rationale is to temporally resolve spectral interferences by slowing down the transfer of heat to the sample. Thus, V (VCl_4 boils at 148°C) would leave the cup earliest, followed by Fe ($FeCl_3$ decomposes at 315°C), Co ($CoCl_2$ boils at 1049°C) and Cr ($CrCl_3$ sublimes at 1300°C). Figure 2 shows the signal recorded at the 267.716 nm channel of Cr for a cup with thick walls (3/16" o.d. with 1/8" i.d. @ 1.5 KW). The signal of Cr appears on the shoulder of a neighboring Fe line (267.688 nm). Even with thick walls, which had been found to maximize the retardation of the appearance of less volatile elements [5], the signals of Cr and Fe were overlapped completely.

Since the cup's geometry could not be used to effect the temporal resolution of spectral interferences, it was decided to maximize the mass of sample per insertion by using cups with the narrowest possible walls (3/16" o.d. with 11/64" i.d.). The plasma's applied power was found to affect not only the shape and intensity of the peaks, but also the transient background. Usually, signal to background ratios (SBR) are maximized as a function of plasma power; however, in this case, SBRs were meaningless because they could not account for the temporal resolution of the signals from their transient background.

For lack of a formal alternative, visual examination of the time profile of signals provided the optimization criterion. The signals obtained at plasma powers of 1.00, 1.25, 1.50, 1.75 and 2.00 kW were examined and it was decided that the best setting to use would be that at which it was easiest to discriminate the peak of interest from surrounding features. For every element, higher power levels resulted in sharper peaks, but because the transient background at the channels of Co and Cr are due to direct line overlaps by Fe and Ag respectively, higher power also meant aggravated spectral interferences. A compromise setting of 1.75 KW was adopted based on these observations.

The complexity of the spectral background over which the signals appeared required the development of more sophisticated exposures than those commonly used in atomic spectroscopy [17]. With unmodified sediments, it had been possible to adequately record time profiles using simple exposures with a single off-line background position [5]. Figure 3 shows the signal that was recorded at the 267.716 nm Cr channel with such an exposure. Sixteen pellets were prepared from a 1:1:5 mixture of AgCl, PACS-1 and graphite, half of the burns were recorded as in Figure 2 and the other half as in Figure 3. The pellets were divided randomly between the two sets, so that the presence of a peak in the second set of exposures could be confirmed from the first.

The off-line position used to record the exposure of Figure 3 had been chosen after careful examination of the first ten frames of Figure 2. To a first approximation, each frame is a wavelength scan and can be used to determine the best position at which to record an off-line background trace. Even with this precaution, the offline background trace could not be used to extract a peak from the online trace of Figure 3, although it can clearly be discerned in Figure 2.

Approximately half of the exposure of Figure 2 was spent recording inconsequential wavelength information. The wavelength resolution of the scans was thus increased, at the expense of their width and of the total duration of the exposure. Exposures were devised for this particular application, that consisted of 50 repeat scans across 32 spectrum shifter positions separated by 0.002 nm centered on the middle of the channel's 0.256 nm span. This was the type of exposure that was used to record the two dimensional profile for the signal of Cr shown in Figure 4. Of the six channels monitored, the signal of Cr was the most difficult to extract from its background. Because the peak of Cr was best demarked from the wing of the nearby Fe line with these exposures, they were used exclusively for the rest of this work.

Signals

The background intensity at the on-line position was calculated by fitting a fourth order polynomial across off-line positions on each side of the peak along the wavelength axis. The signal's baseline was then constructed by interpolation of each wavelength scan's polynomial at the on-line position, across the full duration of the exposure. The corrected signals were obtained by subtracting the interpolated baseline from the on-line trace, point by point. Finally, peak areas were calculated by numerical integration of the corrected signals [17].

The adequacy of numerical integration for the calculation of peak areas has been established [6]. The performance of the baseline correction procedure was evaluated using overlayed 3-D plots. Briefly, a background estimate was calculated for each position of the wavelength scans over the whole duration of the exposures. Axonometric plots of the raw signal and its background estimate were then generated and plotted in two colors. This was especially useful during the development of the baseline correction procedure, to determine the degree of the polynomial that best approximated the shape of the background at a given channel.

The reproducibility of the measurements was poorer than it had been for unmodified sediments. The RSD on peak area for the trace refractories was between 10% and 25%, as opposed to 7% for volatile elements in unmodified sediments [5]. This is due in large part to the combined effect of exacerbated physical and spectral interferences. The volatile elements had boiled off during a quieter period after the insertion of pellets of unmodified sediment, when a stable central channel was formed through the plasma [5]. The simultaneous release of all trace elements, matrix constituents and the additive's cation into the plasma is certain to have resulted in a more turbulent environment for the refractory elements. Visual observation of the counter ion's green plume through the plasma suggested that a shorter entrance slit might lessen the effect of this source of noise.

The absence of detailed theoretical and experimental studies on the basic dynamics of the volatilization process of inorganic compounds [18] and the lack of information on the mineralogical composition of PACS-1 make it difficult to model in detail the chemistry occurring in the DSI probes. Nonetheless, PACS-1 is part of a class of poorly consolidated sediment in which most of the trace elements are not strongly bound to the silicate matrix but adsorbed on the surface of the clay minerals [6], so it is very probable that the vaporization of the low boiling point elements proceeds as a thermal desorption. On the other hand, the chemistry behind volatilization enhancement may involve a series of steps with competing side reactions [8,19,20], and is clearly more complicated. In terms of signals, this is reflected in the inconsistent profile of the transients. The overlayed profiles of the signal of Cr after five replicate insertions of 1:1:5 mixtures of PACS-1, AgCl and graphite are shown in Figure 5. The shape of the peaks is irregular and varies between insertions, in contrast to what had been observed earlier with unmodified PACS-1 (cf. Figure 6).

Calibration

The latter observation bode ill for the calibration of the technique by the method of standard additions, because it suggested that the thermochemical reactions were likely to proceed differently depending on the chemical form of the analyte. Pellets spiked with powdered arc standards (the SPEX g-standards, mixtures of metal oxides and graphite) were prepared as previously reported [6] for the determination of three trace refractory elements by the method of standard additions.

The first encouraging observation was that the shape of the peaks was not systematically different for the spiked samples. We were concerned that the spikes would result in sharp peaks at the start of the burn, increasing with the size of the spike, while the body of the signals remained unaffected. This was not borne out, and based on the information encoded in the shape of the signals, it appeared that the thermochemistry responsible for volatilization enhancement proceeded in a like manner for both the original sample and the spiked samples.

Blank pellets pressed from 1:5 AgCl in graphite were analyzed to check for contamination by the six elements of interest, Al, Co, Cr, Fe, Ni and V. Signals could be discerned from background noise and baseline drift at the channels of Al, Fe, Cr, and Ni. Strictly speaking, reagent blanks are required for the determination of these elements since the background corrected signal is no longer equivalent to a blank corrected measurement [21]. In practical terms, however, the signals of Al, Cr and Fe were at least two orders of magnitude greater than the blanks. Even with a 1σ confidence interval, the background corrected and blank corrected signals were not significantly different for Al and Fe.

The graphs of Figure 7 are plots of peak area vs. concentration for the four trace elements, Co, Cr, Ni and V. Each point is an average of the blank corrected signal from twenty replicate runs. In previous work with volatile elements, the RSD on integrated signals had fallen between 5 and 10 percent, and five replicate insertions had been enough to ensure adequate accuracy [6]. Now, with RSDs between 10 and 25 percent, it was necessary to average more measurements to bring the error on the calibration curve's slope to within the same range.

The determination of Al and Fe was not attempted, because they are major components of the sediment's matrix (Al_2O_3 @ 12% and Fe_2O_3 @ 7%) and it had already been found that large additions of g-standard resulted in systematic errors [6]. The graphite from which the powdered arc standards were prepared does not have the same binding properties as the briquetting graphite. Large volumes of gases were released at once with volatilization enhancers, and weaker pellets were more readily shattered. When the spike of g-standard accounted for nearly a third of the mixture's composition (i.e. 5 parts g-standard : 2 parts AgCl : 2 parts PACS-1 : 5 parts graphite) the pellets started shattering and sizable fragments of material were ejected from the graphite cups. The most concentrated g-standard is 1000 µg/g (0.1 % wt./wt.) which set an upper concentration limit of about 300 µg/g for the standard additions calibration curves.

The results of ten independent determinations are summarized in Table 3. Each determination involved the preparation of twenty pellets from a series of mixtures of PACS-1, AgCl, graphite and g-standard. In each case, an independent calibration curve was plotted and a concentration estimate calculated from its x-intercept. Not only did the spread of the concentration estimates increase with concentration, as reflected by their %RSD, but the two higher concentration estimates were also systematically exaggerated. This is reminiscent of what had been observed for the more concentrated volatile elements in unmodified sediments [6].

Pellets with varying amounts of g-standards were crushed manually as a rough test of their robustness, and the pellets got progressively weaker with increasing additions of g-standard. Weakened pellets should offer less resistance to the initial rush of gases after their insertion, resulting in greater gas velocities out of the probes. In turn, this physical interference would result in shallower slopes for the calibration curves, and exaggerated concentration estimates by the method of standard additions [6].

CONCLUSION

With the proper choice of thermochemical additive, it is possible to determine trace refractory elements such as Co, Cr, Ni and V in sediments using the method of standard additions. It has been found that the effect of AgCl on Co, Cr, Ni and V does not appear to depend on their chemical form. The signals of these elements do not differ in shape between the original sample and the ones spiked with g-standards. Furthermore, the concentration estimates obtained are within 15 % of their certified values for Co and Ni, and within 25% of their certified values for Cr and V.

A word of caution is in order here; PACS-1 is representative of a class of poorly consolidated sediment in which most of the trace elements are not strongly bound to the silicate matrix. The applicability of the standard additions procedure should be checked for each type of sample, to determine whether the thermochemistry responsible for volatilization enhancement proceeds in like manner for the sample and the spiking standard.

TABLE 1

Boiling points of selected refractory elements, their oxides, carbides, chlorides and fluorides(1).

ELEMENT	BOILING POINT (°C)				
	metal	oxide	carbide	chloride	fluoride
Co	2870	> 1795	..	1049	1200
Cr	2672	4000	3800	1300	> 1300
Fe	2750	> 1594	> 1837	280-285	> 1000
Mo	5560	^{s}1155	> 2692	268	35
Ni	2730	> 1984	N/A	973	> 1000
V	3380	^{d}1750	3900	128	111

s - sublimes
d - decomposes

(1)- source : CRC Handbook of Chemistry and Physics, 66th Edition

TABLE 2

Details of powders for pellet DSI

Sediment SRM :	
PACS-1	Marine Analytical Chemistry Standards Program National Research Council (NRCC) Atlantic Research Laboratory Halifax, Nova Scotia, Canada
	Al - 12.23 % as Al_2O_3 Co - 17.5 μg/g Cr - 113 μg/g Fe - 6.96 % as Fe_2O_3 Ni - 44.1 μg/g V - 127 μg/g
Briquetting graphite powder :	
Spectroscopic Electrodes	Bay Carbon Bay City, MI, USA
Thermochemical additive :	
Silver chloride, AgCl, 99.999%	aldrich chemical co. Milwaukee, WI, USA
	elemental analysis : Ag - 75.8% trace analysis : Element μg/g (μg/g) None detected
Powdered arc standards :	
SPEX g-standards	SPEX INDUSTRIES, inc. Metuchen, N.J., USA
	metal oxides in a graphite matrix, 0.0001, 0.001, 0.01 and 0.1 % wt./wt.

TABLE 3

Replicate concentration estimates (in μg/g) determined by the method of standard additions for four refractory trace elements in PACS-1, with AgCl as volatilization enhancer

		Co	Cr	Ni	V
		19.73	147.39	51.39	112.96
		17.61	106.54	43.47	126.25
		16.18	110.80	45.38	205.98
		15.44	133.09	51.63	117.39
		19.09	124.92	51.30	147.85
		15.14	115.64	44.89	180.99
		14.77	141.84	51.27	164.80
		16.82	144.14	41.72	195.99
		20.58	155.57	53.98	122.92
		16.75	163.71	39.40	120.32
average	:	17	134	47	150
%RSD	:	11	14	10	22
error	:	- 1.6 %	18 %	7.6 %	18 %

(1)- spiking standard : SPEX g-standards

(2)- error : $(C_{average} - C_{reference}) / C_{reference}$

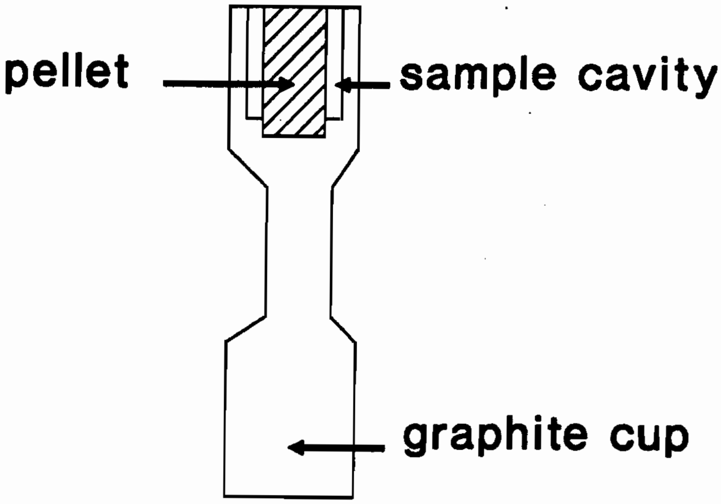


Figure 1
DSI probes consisting of a 125 mg pellet of sample held in an undercut graphite cup, used for the determination of refractory elements in sediment samples using thermochemical additives (o.d. : 3/16", i.d. : 11/64", sup depth : 3/8")

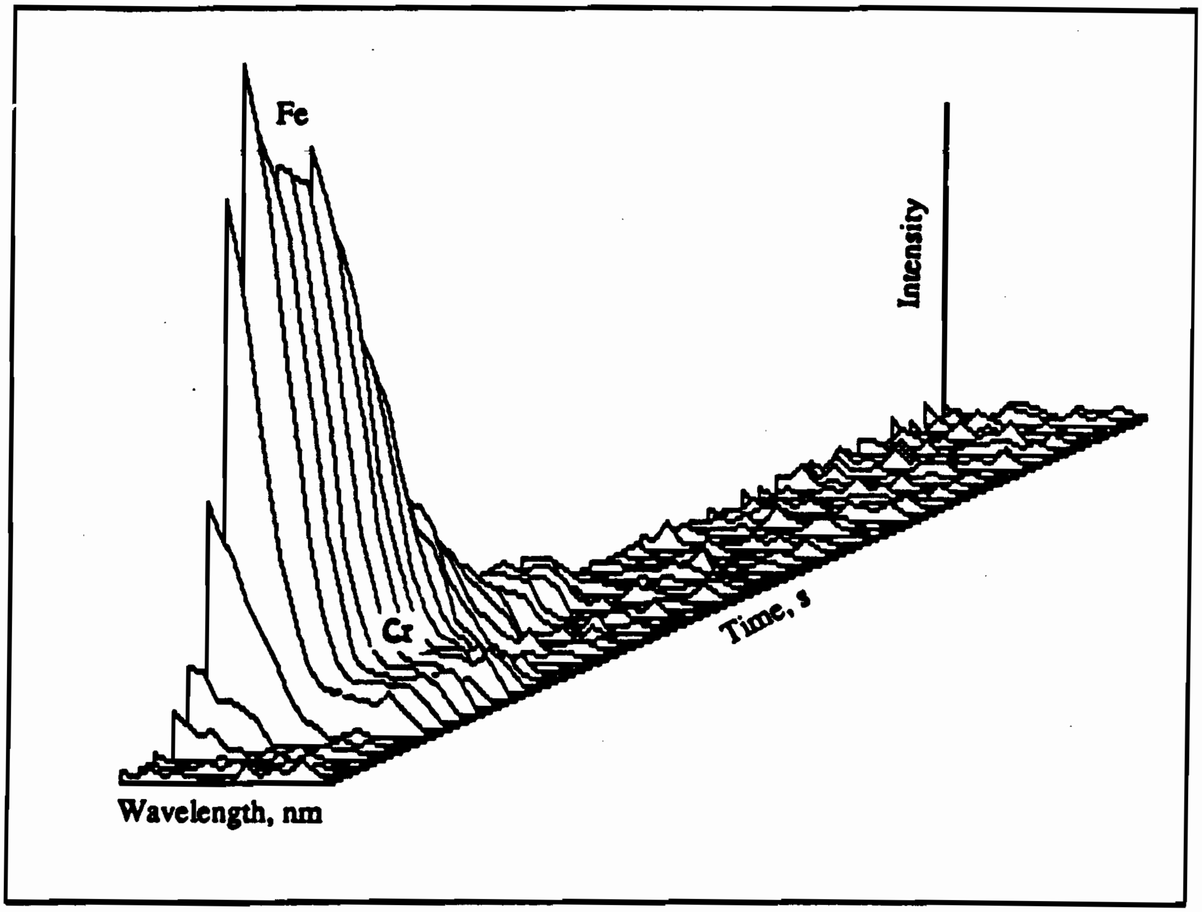


Figure 2

Signal recorded at the 267.716 nm channel of Cr after the insertion of a pellet pressed from a 1:1:5 mixture of AgCl, PACS-1 and graphite.

wavelength span : 0.075 nm
duration : 20 s

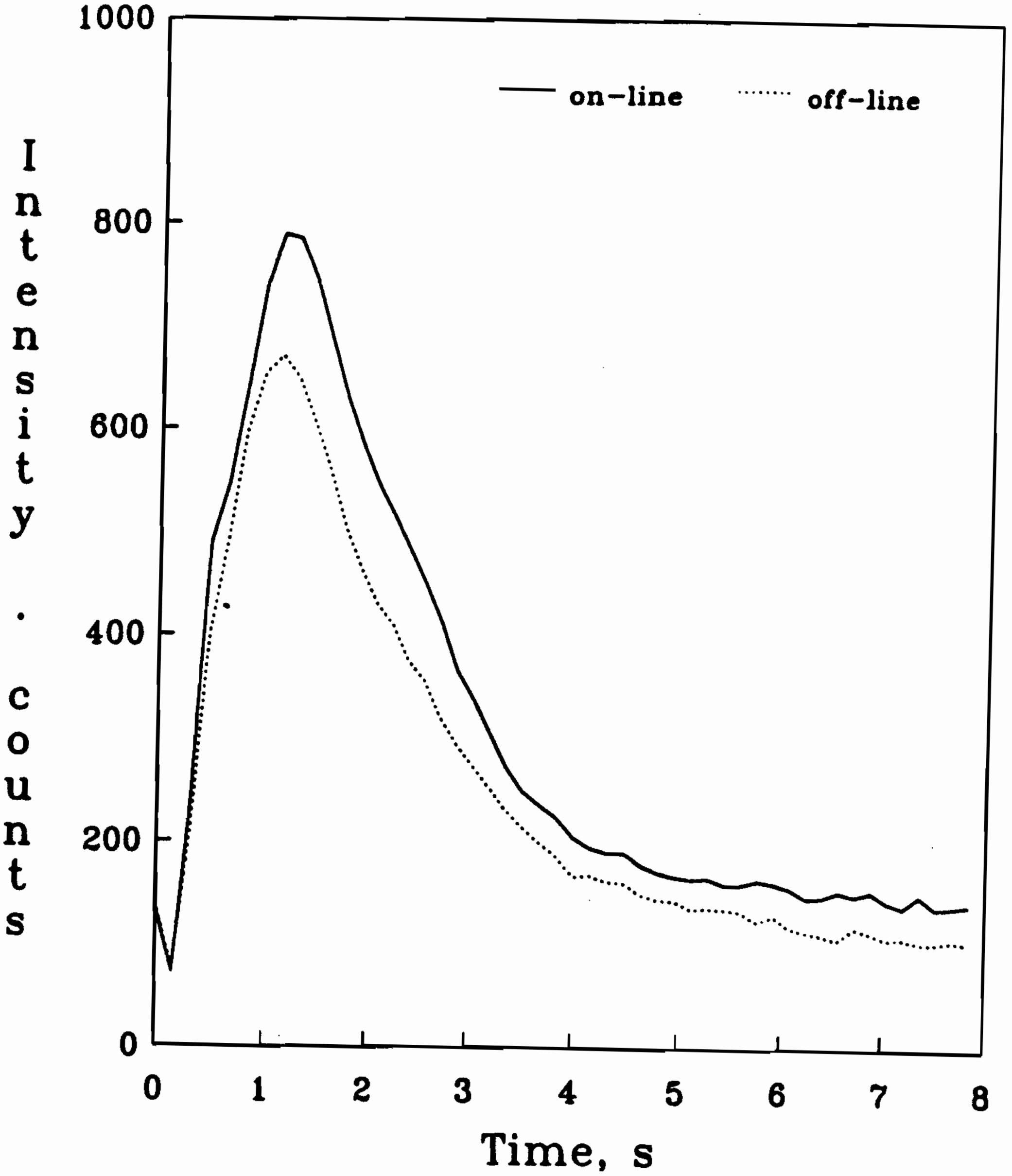


Figure 3

Signal recorded at the 267.716 nm channel of Cr using a simple exposure with a single off-line background position.

on-line : 267.716 nm

off-line : 267.707 nm

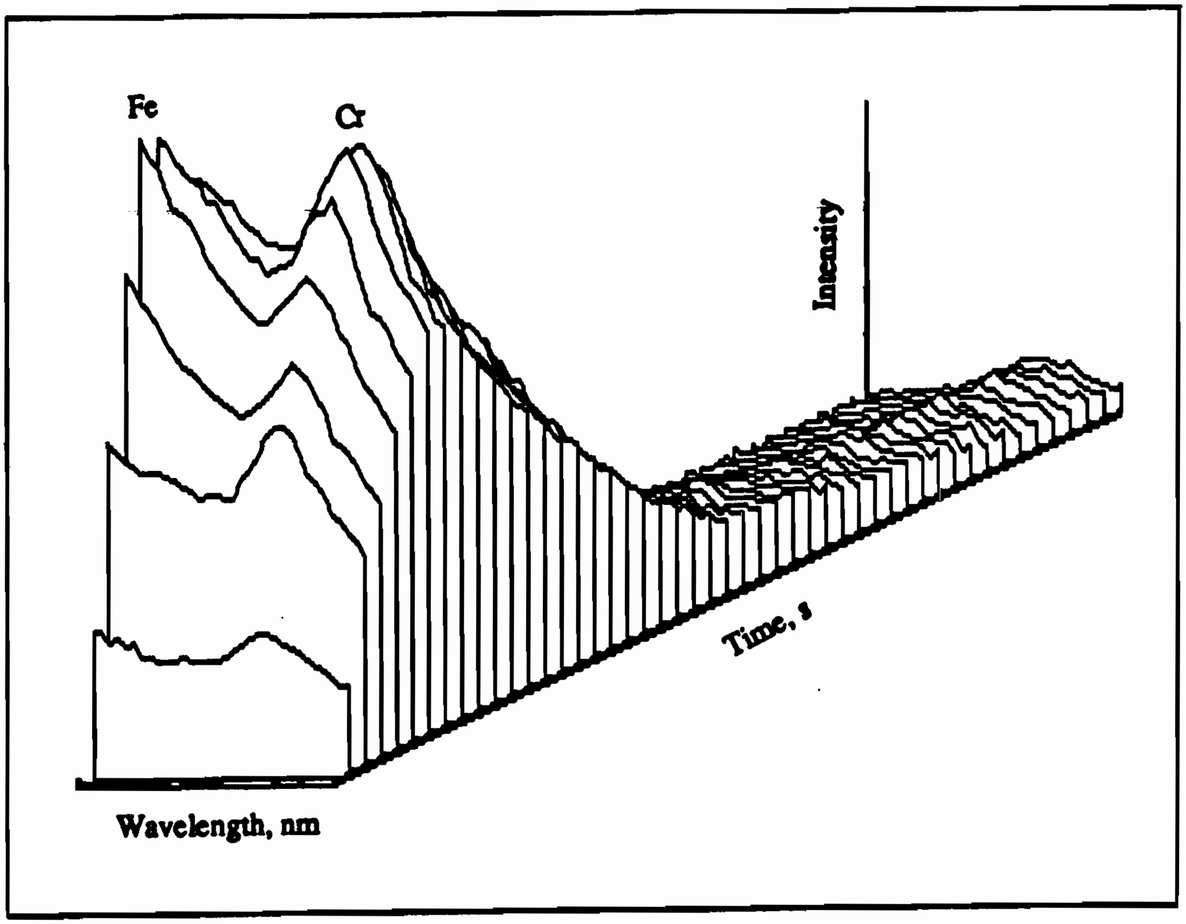


Figure 4

Signal recorded at the 267.716 nm channel of Cr using an exposure consisting of 50 repeat scans across 32 spectrum shifter positions separated by 0.002 nm.

duration : 10 s

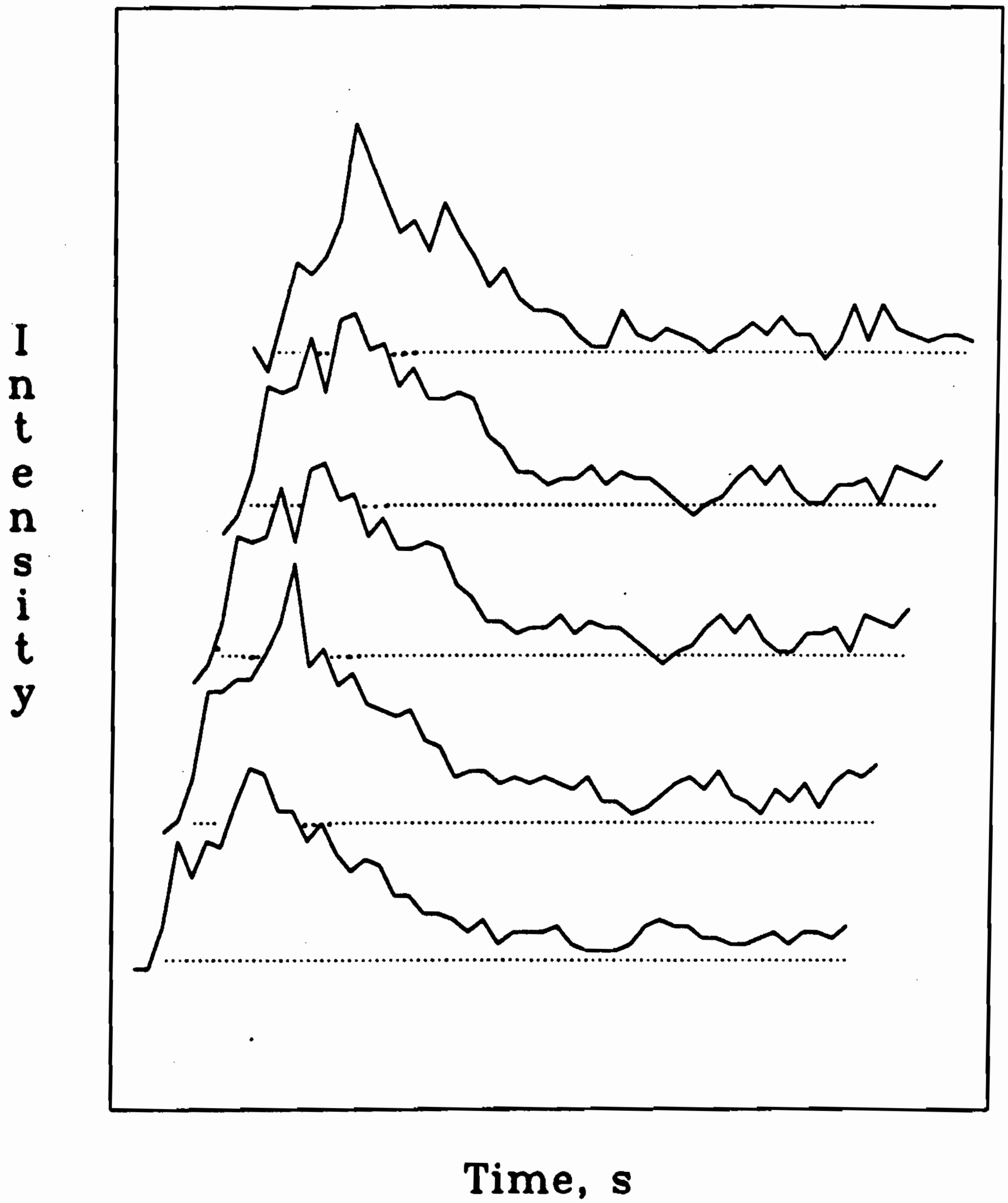


Figure 5

Offset replicate signals for Cr, after the insertion of 5 pellets pressed from a 1:1:5 mixture of AgCl, PACS-1 and graphite. RSD on peak area : 13%

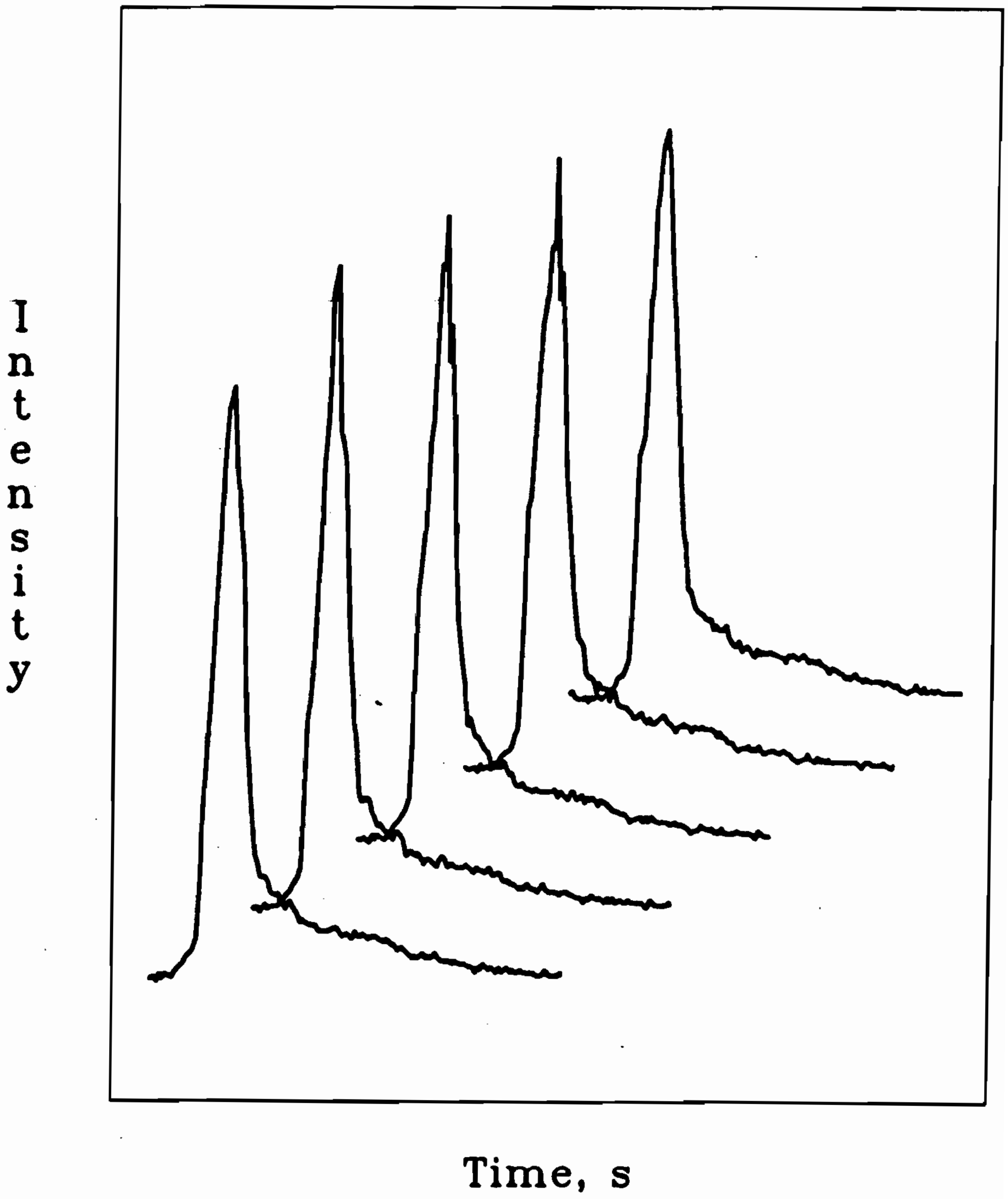


Figure 6

Offset replicate signals for Zn, after the insertion of 5 pellets pressed from a 1:5 mixture of PACS-1 and graphite.
RSD on peak area : 7%

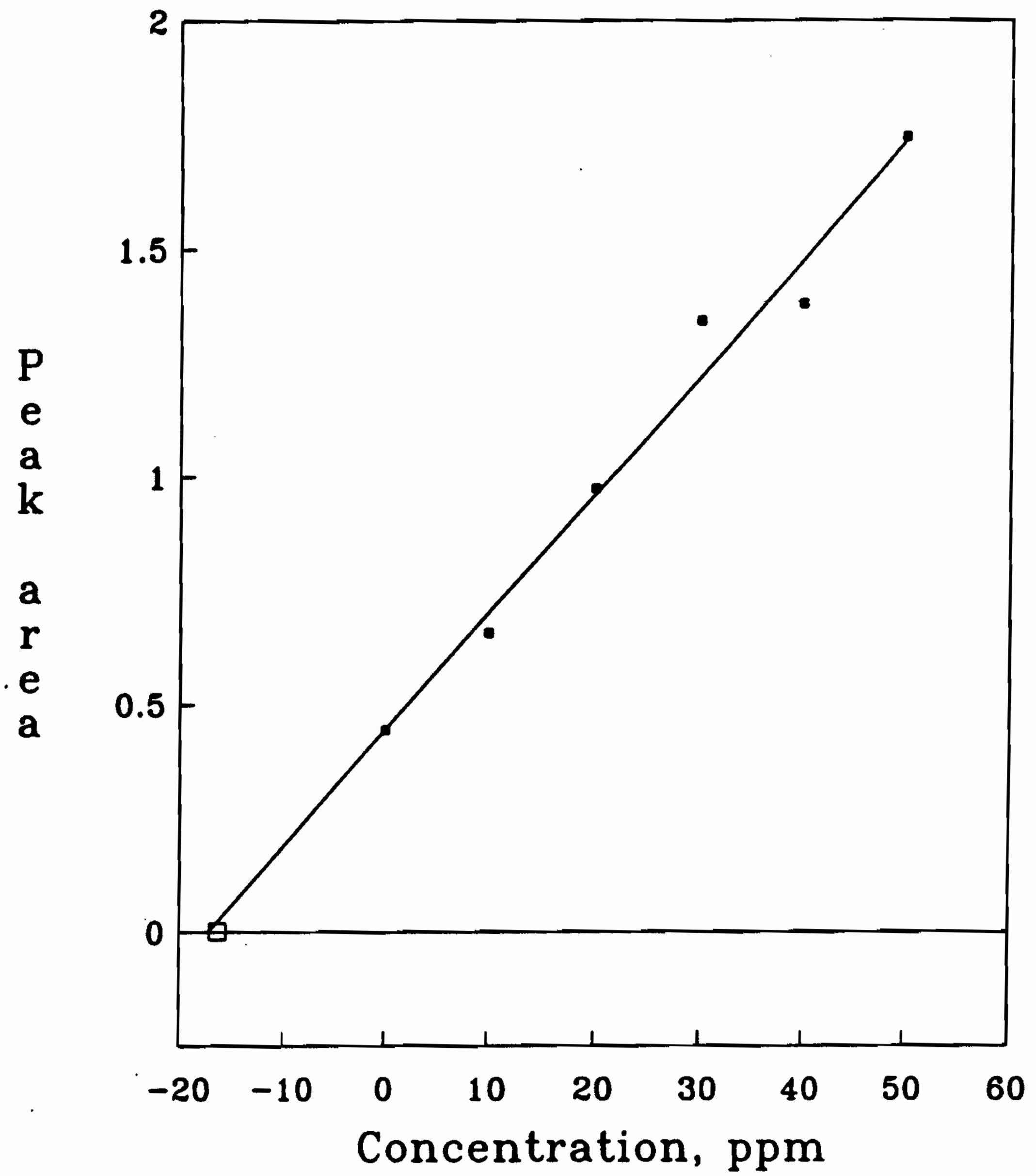


Figure 7.a)-
Calibration curve obtained by the method of standard additions for Co
slope = (2.5+/-0.2)x10^4

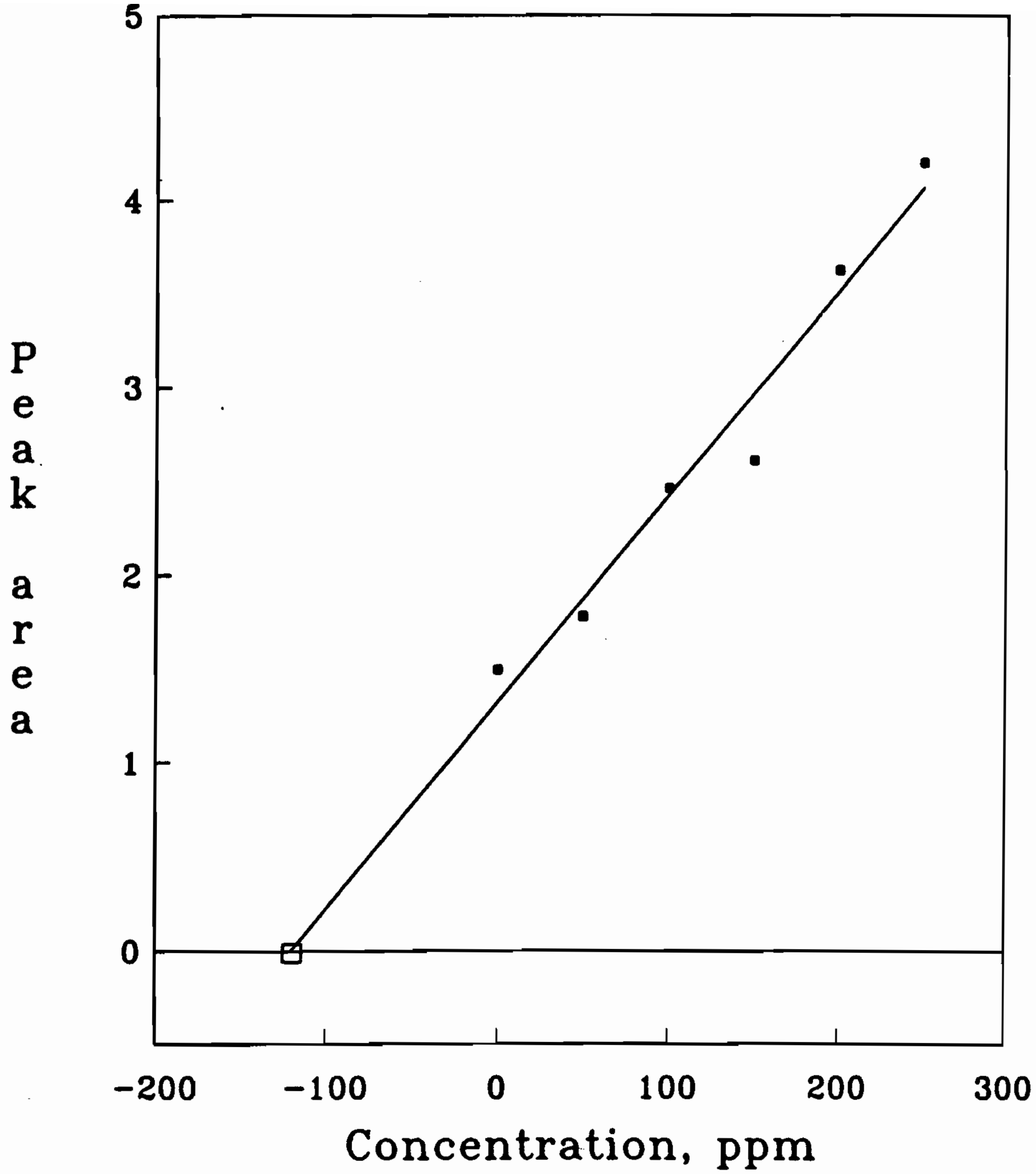


Figure 7.b)-

Calibration curve obtained by the method of standard additions for Cr

slope = (1.1+/-0.1)x10^4

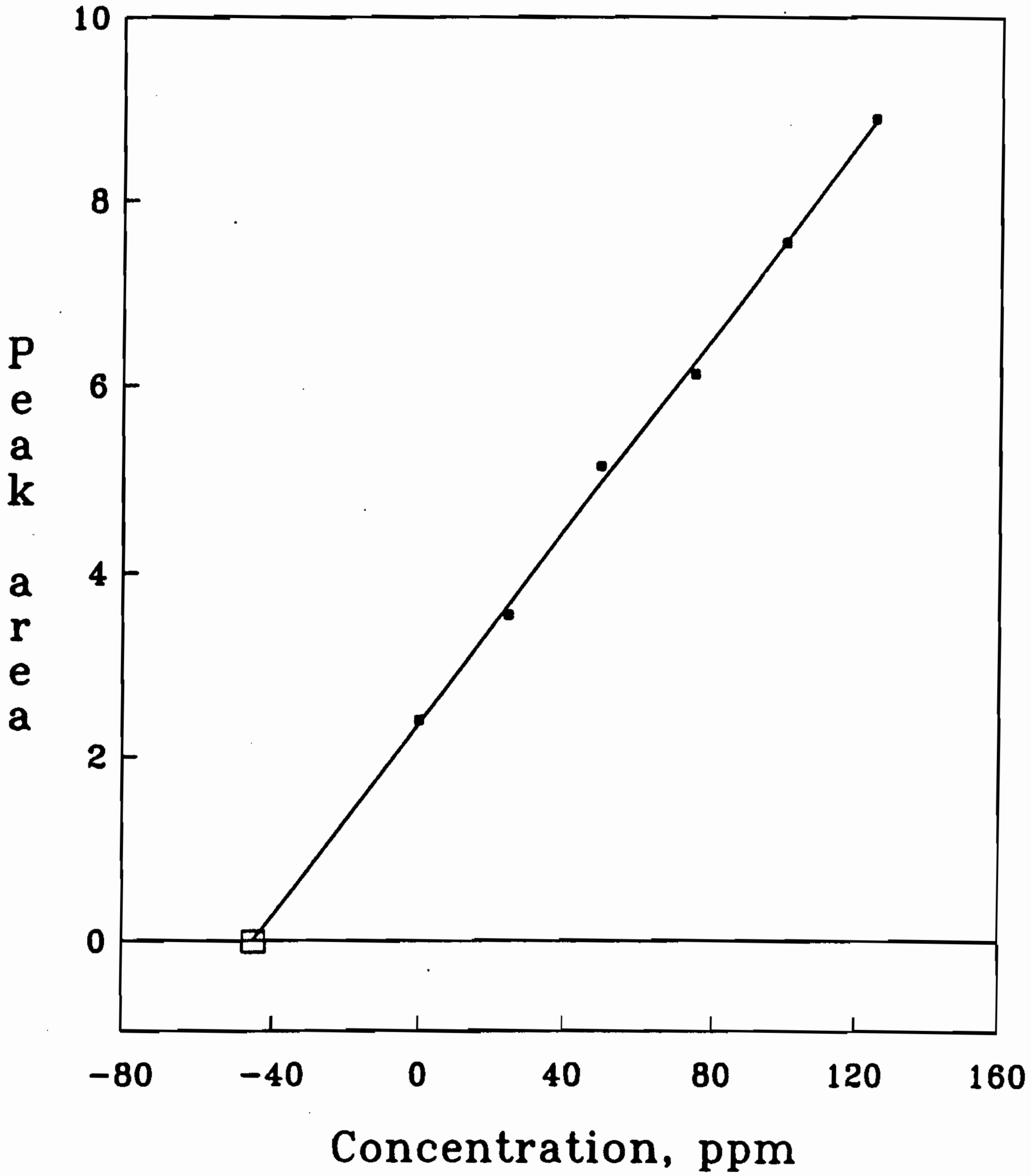


Figure 7.c)-
Calibration curve obtained by the method of standard additions for Ni
slope = (5.2+/-0.1)x10^4

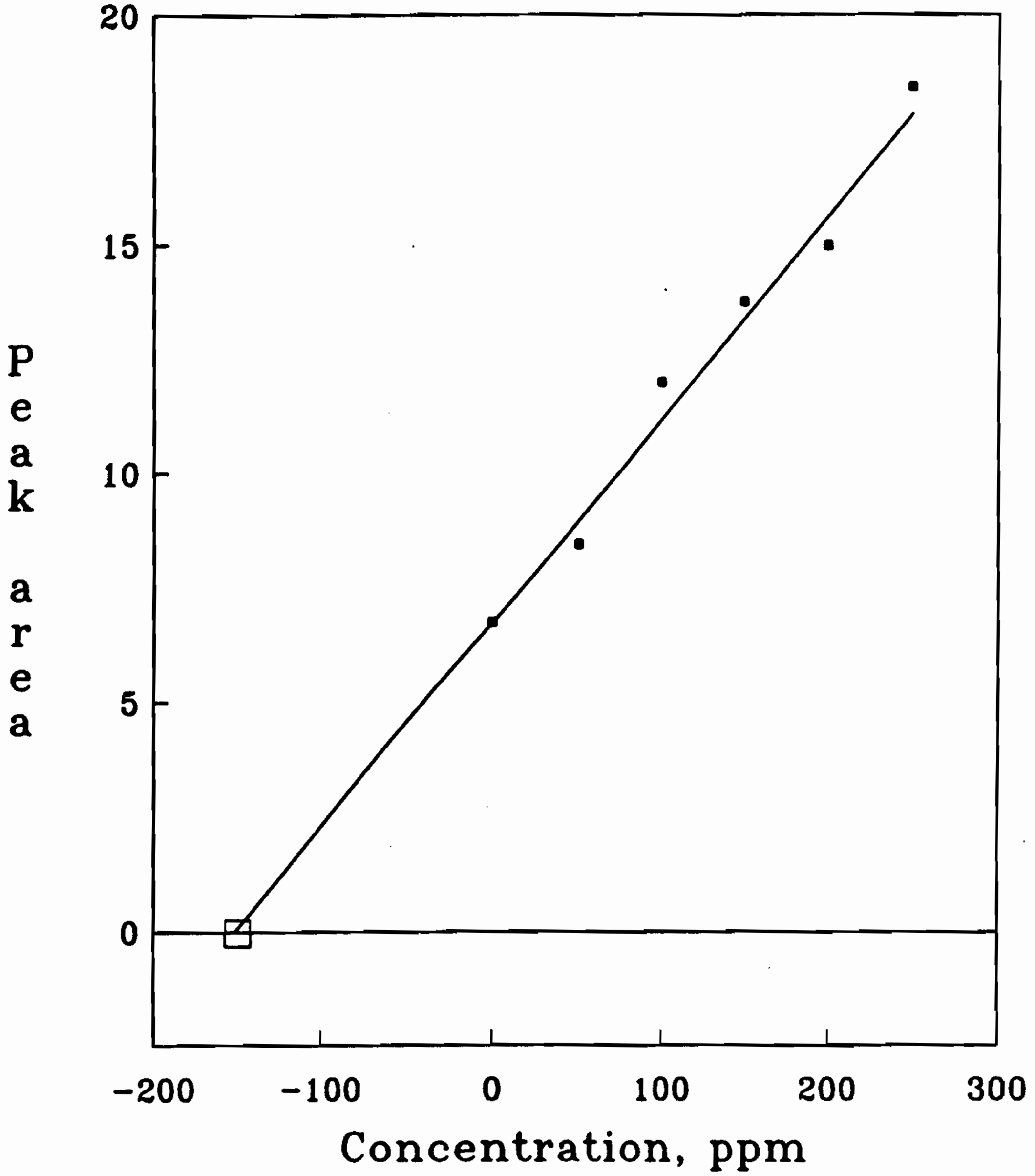


Figure 7.d)-

Calibration curve obtained by the method of standard additions for Co

slope = (4.4+/-0.4)x10^4

REFERENCES

1)- C.W. McCleod, P.A. Clarke and D.J. Mowthorpe, *Spectrochim. Acta* **41B**, 63 (1986)

2)- W.E. Pettit and G. Horlick, *Spectrochim. Acta* **41B**, 699 (1986)

3)- Y. Shao and G. Horlick, *Appl. Spectrosc.* **40**, 386 (1986)

4)- G. Zaray, J.A.C. Broekaert and F. Leis, *Spectrochim. Acta* **43B**, 241 (1988)

5)- L. Blain and E.D. Salin, *Spectrochim. Acta* to be published

6)- L. Blain and E.D. Salin, *Spectrochim. Acta* to be published

7)- I.B. Brenner, A. Lorber and Z. Goldbart, *Spectrochim. Acta* **42B**, 219 (1987)

8)- G. Zaray, J.A.C. Broekaert and F. Leis, *Spectrochim. Acta* **43B**, 241 (1988)

9)- M. Reisch, H. Nickel and M. Mazurkiewicz, *Spectrochim. Acta* **44B**, 307 (1989)

10)- A.G. Page, K.H. Madraswala, S.V. Godbole, M.J. Kulkarni, V.S. Mallapurkar and B.D. Joshi, *Fres. Z. Anal. Chem.* **315**, 38 (1983)

11)- A.G. Page, S.V. Godbole, K.H. Madraswala, M.J. Kulkarni, V.S. Mallapurkar and B.D. Joshi, *Spectrochim. Acta* **39B**, 551 (1984)

12)- G.F. Kirkbright and Z. Li-Xing, *Analyst* **107**, 617 (1982)

13)- V. Karanassios, M. Abdullah and G. Horlick, *Spectrochim. Acta* **45B**, 119 (1990)

14)- R.L.A. Sing and E.D. Salin, *Anal. Chem.* **61**, 163 (1989)

15)- P. Burgener and G. Légère, *ICP Info. Newslett.* **13**, 521 (1988)

16)- L. Blain, E.D. Salin and D.W. Boomer, *J. Anal. At. Spectrom.* **4**, 721 (1989)

17)- L. Blain, Doctoral dissertation, Department of Chemistry, McGill University (1991)

18)- E.R. Prack and G.J. Bastiaans, *Anal. Chem.* **55**, 1654 (1983)

19)- H. Nickel, *Spectrochim. Acta* **23B**, 323 (1968)

20)- J. Bril, *Spectrochim. Acta* **23B**, 375 (1968)

21)- J.D. Ingle and S.R. Crouch; **Spectrochemical Analysis**; Prentice Hall, inc.:Englewood Cliffs, NJ (1988)

CHAPTER 6

Conclusion

The fireball of the inductively coupled plasma provides a very energetic environment which can be used to vaporize analytes from solid samples directly. Pellets weighing up to 250 mg have been inserted into the plasma's core without extinguishing it. This hot core is where inductive energy transfer occurs from the load coil to the plasma's support gases, and it is the region of greatest gas velocity. This feature can be used advantageously to confine the flow of analyte vapors in a channel through the plasma. Indeed, many reports have noted the importance of insertion depth in direct sample insertion. When pellets pressed from mixtures of graphite based metal oxide standards were inserted deep enough into the plasma that the latter could reform around their base, visual examination of the plasma revealed that the elements giving rise to visible emission (Si mainly) were contained in an axial channel through its tailflame. When the insertion was not as deep into the plasma, the fireball could be seen to ride on top of the pellet and the visible emission appeared as a diffuse glow around the plasma's periphery.

These observations support the view that the plasma is capable of directly handling solids. After all, the solids were only held in a wire loop because gravity would not allow the pellet to remain in the plasma by itself. The probe of DSI had become the sample itself, albeit dispersed in a briquetting graphite binder to ensure its cohesion. As a practical benefit, the increased mass that could be inserted in the plasma this way resulted in commensurate improvements in detection limits and precision.

The requirements of the ideal emission source are worded very broadly, `"... it should be capable of handling liquids, solids and gases ..."`. Few of the solids that analysts have to work with are as simple as mixtures of metal oxides in graphite powder. Most have complex matrices that are refractory to thermal and chemical treatment, and their assay involves many hours of labor. To truly demonstrate its power, the ICP should be able to handle directly a fragment of rock or a chip of superconducting ceramic. As a step in that direction, a sediment reference material was mixed with briquetting graphite and pressed into pellets which were then inserted into the plasma held in wire baskets.

The matrix of sediments is not thermochemically inert, large volumes of gases are released upon insertion of pellets prepared from mixtures with a proportion of sediment as low as one part in ten parts graphite. The fireball cannot adjust to this sudden rush of gases, let alone contain it in a central channel through the tailflame. When the plasma wasn't extinguished, it glowed orange and it seemed as though the support was no longer argon gas but silicon vapors.

The next best thing to directly inserting a fragment of sample in the plasma is to pack it in a graphite cup and insert that in the plasma. When this was tried with sediment, the large volumes of gas released upon insertion ejected much of the powder into the body of the plasma and the effect was akin to fireworks. When the plasma settled back down, orange silicon emission glowed through the plasma's tailflame for more than five minutes. When the probe was retracted from the plasma, it was found that a small glass globule had formed in the bottom of the cup's well. The rich matrix of sediments thus provides many competing thermochemical reactions to vaporization. The cure is well known from dc arc experience, mixing with a thermochemically inert binder like alumina or graphite. To be fair to the ICP, any thermal source would experience the same problems and the defect is with sample presentation rather than the plasma itself.

By binding the sediment in a graphite pellet, the powder was kept in the cup upon insertion and the formation of a refractory glass globule was prevented. It was then possible to push the probe assembly directly into the plasma, and the walls of the graphite cups prevented the rushing gases from invading the fireball. The orange emission of silicon was contained in an axial channel through the plasma, albeit a turbulent one. The observation that a short quiet period preceded the onset of orange emission suggested that the walls of the cup acted as heat barriers, and might thus be used to separate temporally the signals of volatile elements from the turbulence brought about by the decomposition of the silicate matrix.

The optimization of a few instrumental parameters, chiefly the thickness of the graphite cup walls, plasma RF power, and the dilution ratio of sediment in graphite, resulted in smooth burns. During the first few seconds it took for the probes to heat up to the decomposition temperature of the silicate matrix, a dark quiet central channel was formed in the plasma. During this period, sharp peaks were recorded for elements of high and intermediate volatility, on quiet baselines. Indeed, the temporal resolution of the signals of interest from spectral interferences was such that a single off-line background position was sufficient for baseline subtraction.

The signals resulting from the insertion of three different sediment reference materials were compared, and it was found that the response factors for the volatile elements varied systematically. It was found that methodological cures such as internal standards and standard additions provided adequate correction. Finally, the accuracy for the determination of volatile elements was on par with what conventional ICP systems offer.

It has thus been demonstrated that the ICP can handle solids, even those that release large quantities of matrix constituents, without seriously degrading its analytical potential. The limits of detection remain in the low µg/g range, although they are higher than what was initially reported with simpler matrices. The precision of the measurements is acceptable, probably more a function of sampling statistics than the plasma's performance. Some objections remain to the routine implementation of DSI for geological analyses, chiefly that the range of elements it can handle is too limited and that sediments are not very representative of geological samples.

The work done with thermochemical additives indicates that the range of elements covered by this technique can be expanded to include refractory metals and those that form refractory carbides with the surrounding graphite. It was found that the most widely proposed volatilization enhancer, NaF, could not be used with sediment because it also promoted the decomposition of silicates and flooded the plasma with silicon. The addition of AgCl results in burns that are smooth enough to keep the plasma lit, although it is obviously taxed by the sudden rush of gases out of the probe.

The ability of the ICP to withstand the intrusion of a solid probe is limited by its gas dynamics. When the release of vaporized material from the probe is sudden or very substantial, as happens with silicon when the matrix of sediments decomposes, the hot core can no longer contain the foreign gases in an axial channel through the tailflame. The chemical and physical integrity of the plasma is impaired, and its performance severely degraded. The ICP thus falls short of the exacting demands atomic spectroscopists have placed on the ideal emission source.

In practical terms, the technique of direct sample insertion is promising for the rapid semiquantitative determination of elements of high an intermediate volatility. Provided an internal standard is used, this technique could be applied to the routine assay of well characterized materials. Whether the additional effort involved in preparing spiked samples for analyses by the method of standard additions is deemed worthwhile will depend on the alternatives. At any rate, it is possible to obtain concentration estimates with relative errors of less than 10% within an hour for powdered samples. Most of this hour is spent mixing powders and pressing pellets one at a time, which both lend themselves readily to automated batch processing.

At present, there are three directions we would like to see DSI take. The first is toward greater automation of the sample preparation procedure, because economy of time is a major benefit of this technique. There is a void of theoretical and empirical data on volatilization and atomization mechanisms which should be addressed. Such data would provide valuable insight into the physics of energy transfer between the plasma and the probe, which would be a valuable asset for the design of novel probes. A better understanding of the thermochemistry that occurs in the graphite cups would allow their full use as crucibles for in situ chemical modification.

CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

1. A DSI probe consisting of a pellet held in a wire loop was developed. This probe permitted the mass of sample inserted in the ICP to be increased without encroaching on the induction zone of the discharge.

2. It was shown that increasing the mass of sample inserted in the plasma resulted in commensurate improvements of detection limits.

3. It was shown that a lower mass threshold sets the effective limit of determination for solid analyses. It was also shown that this limit is fixed in absolute terms. Increasing the mass of sample consumed per analysis effectively increased the mass of analyte used for a given concentration, and this was shown to improve the precision of the technique at lower concentrations.

4. It was shown that sediment samples release too much material at once in the plasma to be inserted as simple pellets held in wire loops. The walls of the graphite cups were found to be necessary to contain the escaping gases in an axial channel through the plasma.

5. It was shown that the graphite cup's geometry can be optimized to temporally resolve the signals of volatile elements and those of intermediate volatility from physical and spectral interferences by matrix constituents.

6. It was shown that fluorinating reagents are not adequate volatilization enhancing thermochemical additives for sediment samples. These

reagents not only enhance the vaporization of refractory elements, but also decompose the silicate matrix and result in aggravated physical and spectral interferences.

7. The method of internal standardization was found to correct differences between the response factors of three volatile elements in three sediment standard reference materials.

8. It was shown that the method of standard additions can be used to perform the determination of six elements of high and intermediate volatility in mixtures of sediment and graphite, using powdered arc standards for the concentration spikes.

9. It was shown that the method of standard additions can be used for the determination of four refractory elements in mixtures of sediment, graphite and AgCl, using powdered arc standards for the concentration spikes.

APPENDIX A

Sample preparation

1)- GENERAL DESCRIPTION :

Once a sample is dissolved, it is easy to process it. Virtually any volume of the solution can be accurately measured, dispensed and diluted with volumetric glassware. As long as the dissolution medium is soluble in the final solvent, mixing occurs almost instantaneously when the two come in contact. Powders are not as easy to handle, and great care must be taken when weighing and mixing them to ensure that the dilution ratio of one in the other is accurate and reproducible. The preparation of powder mixtures and pellets has been discussed in various parts of the thesis (cf. pages 57,60,61,79,80,81,116 and 117), however for the sake of clarity and because it is an important aspect of this work, these piecemeal descriptions are compiled in this appendix.

2)- MIXING POWDERS

To be suitable, the mixing procedure should produce a powder that has a reasonably constant composition for aliquots of a given mass. The smaller the mass of mixture used in the end, the more stringent the demands on the mixing procedure. In practical terms, a mixing procedure that did not enhance the pellet to pellet variance on peak area for mixtures of SPEX G-standards, compared with that of straight G-standards, was considered adequate for this work.

The variance of peak area with pure G-standards was about 7% (cf. Chapter 2, page 60), and this was the goal that was set for mixed standards prepared from G-standards and briquetting graphite. It was found that for pellets of 125 mg and more, the best procedure was to weigh both powders into a 60 cc plastic mixing chamber (Nalgene bottle), to which 10 plastic mixing beads (1/4" dia.) are added, and to agitate manually for 5 minutes. Using this procedure, the variance on peak areas and peak heights for mixed standards were about the same as those usually obtained with undiluted G-standards in our laboratory.

A balance with two operating modes was used for this work, in the semi-micro mode this balance can only handle up to ### g but it offers a resolution of 0.00001 mg, while in the other mode it can take up to ### g with a resolution of 0.0001 mg. For the mixing operation, large enough masses of powder were used that the resolution of the second mode was sufficient. Mostly, 1 to 4 mixtures of sediment in briquetting graphite were prepared from which 15 pellets of 125 mg could be pressed. The smallest weight to be measured was thus 375 mg, with a resolution of +/- 0.03%.

The interested reader is referred to pages 60 and 61 for a discussion of the shortcomings of the 5100 SPEX mechanical mixer/mill, which was found to perform well as a grinder but rather poorly as a mixing device for this application. However, mechanical mixing is not ruled out and this operation could easily be automated. What is needed is to devise a mechanical mixer that can handle larger containers, so that 10 or more mixing beads can be used, with an arm motion that is not as smooth and rhythmic as that of the 5100 SPEX mixer/mill.

3)- PRESSING PELLETS

The mixtures of powdered standards and briquetting graphite were pressed into pellets with a manual press of the kind used in calorimetry (cf. Table 1 of Chapter 2), using custom made hardened steel punch and die sets. To keep the construction of the punch and die sets simple, their diameters were kept in common North American machining units (i.e. 1/8", 3/16", 1/4", 5/16" and 3/8").

It was found that the cohesion of the pellets was improved when the mixed powders were dried overnight in a 60°C oven. This mild pre-heat did not result in volatility losses for either As or Hg, the two most easily lost elements, as was verified by comparing the average peak area for pellets prepared from an untreated mixture and one subjected to this pre-heat.

Cross-contamination is a nagging difficulty with powders, because the sample preparation equipment cannot be conveniently rinsed. A simple cleaning procedure was devised whereby the punch and die sets are cleaned with a round brush with stiff bristles, such as those used to clean burettes, followed by five blank pressings. The fifth pellet is inserted to check for cross-contamination. This procedure was found to work well until the punch and die sets had been used long enough that the surface of the die had become scarred. This usually became a problem after pressing between 400 and 600 pellets.

4)- STANDARD ADDITIONS

The usual procedure for standard additions is to analyze the sample, then spike it with small volumes of concentrated standard and analyze it again until enough points are obtained to establish a calibration curve.

With powders, it is more convenient to prepare batches of pellets ahead of time, so for each analysis five batches of pellets were prepared as in the example given below.

The G-standards that were used to spike the samples come in seven steps (0.0001%, 0.00033%, 0.001%, 0.0033%, 0.01%, 0.033% and 0.1%) for every element but the internal standard (In @ 0.1%). The standard additions samples were prepared by adding a variable weight of G-standard of appropriate concentration to the mixture of sediment (PACS-1) and briquetting graphite.

To keep the proportion of sediment matrix constant in the mixtures, the amount of graphite was adjusted for each addition of G-standard. For example, the calibration data for Cd in Figure 4-a) goes from 0 to 10 µg/g in four increments :

mixture concentration	mass of graphite (mg)	mass of G-standard (mg)	G-standard used
0 µg/g	3.000	0	
1 µg/g	2.950	0.050	0.001%
2 µg/g	2.900	0.100	0.001%
4 µg/g	2.940	0.060	0.0033%
10 µg/g	2.950	0.050	0.01%

The total weight of sample per batch was about 3.5 g, from which between fourteen and sixteen 225 mg pellets could be pressed.

It was found that adding more than 125 mg of G-standard significantly weakened the pellets, which favored the use of higher concentration G-standards. On the other hand, weighing, transferring and mixing small masses of powders are difficult even with a semi-micro balance, and a lower threshold of 50 mg of powder was adopted. This entailed a compromise in the choice of the spiking standard, and explains why the 4 µg/g spiked mixture was prepared with 33 µg/g G-standard but the 10 µg/g spiked mixture with 100 Og/g G-standard.

It is difficult to weigh out exactly 50 mg of powder, so the weight of each addition was recorded and the spiked mixture's concentration adjusted. The reproducibility of the signals was used as a check on the mixing operation and the RSD on peak area was again 7%. The higher concentrations were problematic because the maximum concentration for G-standards is 1000 µg/g, which entailed the use of large additions that resulted in weaker pellets.

APPENDIX B

Spectrometers

1)- GENERAL DESCRIPTION :

Two polychromators were used for this work. The first was a commercial instrument, the Thermo Jarrell Ash ICAP 61 direct reader. Two processors control the operation of this instrument, an IBM AT compatible microcomputer and an on-board controller. The commercial version of the ICAP 61 software interface was found lacking in flexibility for the acquisition of transient signals [1]. Although the controller's instruction set was not as restrictive, it remained difficult to acquire enough points at more than one spectrum shifter position to record adequately the transient signals and an off-line background for baseline correction [1].

A software interface was written in Turbo Pascal to send directly control codes to the instrument's on-board processor through the serial port of the IBM AT. These programs were written in collaboration with Lyne Gervais, who has already presented it in Appendix F of a Master of Science thesis [2]. The first program, SETUP, was written by Laurent Blain [3]. It is used to establish a method for data acquisition by specifying the channels to monitor, spectrum shifter positions, flush time, integration time and number of cycles. The data acquisition program, EXPOSUR2, was written in collaboration with Lyne Gervais [3], it controls the instrument based on the data acquisition protocol specified in a method established with SETUP, and stores the data on disk.

The other spectrometer was an upgraded Jarrell Ash ATOMCOMP 97500 direct reader [4]. Table 1 in chapter 3 lists the important instrumental features of this instrument. The SCANG program for this system comes in two parts, a memory resident assembly language driver and a user interface written in the C language [5]. The source code of the assembly language driver was provided with the instrument and minor modifications were made to accommodate custom exposures and interface with the direct sample insertion device's controller via the RS-232 serial port COM1.

A multiple integration time base was implemented at Technical Service Laboratories at our suggestion and provided as a software upgrade. This upgrade allowed a different integration time for each channel, with the spectrum shift option still available. The basic idea is to split the integration of the signals between hardware and software. A short integration time is used in hardware as the spectrum shifter positions are repeatedly scanned, and counters associated with each channel are incremented after each scan. Every channel has its associated section of the data array and a set of registers in a control array. For a given channel, the counts read in from the channel card are summed in the current segment of their section in the data array until the scan counter reaches a preset value (i.e. the number of scans that must be summed in memory to make up the effective integration time given the operational integration time). When the scan counter has reached that value, the program increments the register that holds the starting address of the current segment in the channel's section of the data array. Once the section of a given channel is filled, data acquisition proceeds as before for all the channels except that the data for that given channel is not stored in the array. This algorithm is the product of a collaboration between Laurent Blain and Guy Légère, its implementation is proprietary to Technical Service Laboratories.

The interface to the controller of the direct sample insertion device (DSID) was provided by adding three short segments of assembly language code to the data acquisition driver. The DOS function calls 3F and 40 were used to read from and write to the standard auxiliary device (AUX:, file handle : 0003H) respectively, using the INT 21 call to DOS [6]. When the data acquisition procedure is called, a code is sent to the DSID and execution is halted until a suitable return code is received, signifying that the DSID is present and properly initialized. If the code returned is not the expected one, an error message is displayed on the controller's screen and the procedure terminates. Later, when the data acquisition procedure has initialized all its functions and is ready to record an exposure, another code is sent to the DSID and execution is halted again until a suitable code is read in, signifying that the insertion has been triggered. When the correct return code is received, the data acquisition program resumes its normal operation. Otherwise, a message informs the user of a synchronization error and the procedure terminates. The details of the communication protocol are discussed in appendix B.

2)- EXPOSURES

The SPECTRUM SHIFT instruction of the ICAP 61 was used exclusively because it was the only procedure that could record more than one point at more than one spectrum shifter position. The TIMESCAN instruction, for example, can record up to 100 consecutive points but at only one spectrum shifter position. In the conventional application of SPECTRUM SHIFT, the wavelength window of the channels can be profiled in as many as 64 steps. The program SETUP was used to define a method which recorded the intensity at two spectrum shifter positions 32 times. The version of EXPOSUR2 used here stored the raw counts directly in a text file, which could then be imported into a spreadsheet.

The TRANS option of SCANG is well suited for the acquisition of transient signals. The commercial version allows up to 128 sequential measurements to be recorded at each of 50 channels. If only a single spectrum shifter position is used, this exposure is equivalent to the TIMESCAN exposure offered by the ICAP 61, except that it offers shorter integration times and 128 points instead of 100. As more spectrum shifter positions are scanned, the number of points that can be recorded at each position drops in proportion. For the conventional on-line / off-line sequence, this amounts to a SPECTRUM SHIFT exposure with twice the number of points. Given the system's multiple integration time base, this was a very satisfactory exposure for the work with the SPEX g-standards and would also be satisfactory for the routine determination of volatile elements in sediments (cf. chapter 3).

The advantage of having access to the source code of the assembly language driver was that the data array could be reallocated, and more memory could be assigned per channel at the expense of the number of channels that could be monitored. This proved essential for the development work with sediments, when it was difficult to discriminate analyte signals from background features. With more memory allocated to each channel, it was possible to record many successive wavelength scans across up to 32 spectrum shifter positions (cf. chapters 3 & 5). The reallocation of the data array was accomplished by changing the value of two constants in the variable declaration segment of the driver : the maximum number of points per channel, and the maximum number of channels.

3)- CALIBRATION OF THE SPECTRUM SHIFTER

The wavelength increment per step of the spectrum shifter was calibrated for the 228.802 nm Cd channel, and assumed to be reasonably constant over the direct reader's focal curve. Strictly speaking, every channel should be calibrated individually since the refractive index of quartz changes with wavelength in the U.V.. The Cd 228.802 nm channel is convenient because of a spectral overlap by As at 228.812 nm, which is of similar intensity.

Wavelength scans were recorded at the 228.802 nm channel when standard solutions of As and Cd were run with a convention nebulization system. The spectra were overlayed and the distance between their maxima determined, in units of spectrum shifter positions, and then converted to nanometers :

position of As 228.812 nm peak : 66
position of Cd 228.802 nm peak : 61
distance in nm : 0.010 nm
distance in positions : 5
resolution (nm/position) : 0.002

It was later found at other channels that the predicted wavelength of nearby spectral interferences could be used to corroborate the assignment of the interferent based on the sample's composition (i.e. mostly minor lines of Fe). For practical purposes, this estimate resolution was deemed acceptable.

4)- REFERENCES

1. L. Blain, E.D. Salin and D.W. Boomer, *J. Anal. At. Spectrom.* **4**, 721 (1989)
2. L. Gervais, Master of Science thesis, Department of Chemistry, McGill University (1989), APPENDIX F - page 127
3. L. Gervais, Master of Science thesis, Department of Chemistry, McGill University (1989), Acknowledgements - page vi
4. P. Burgener and G. Légère, *ICP Info. Newslett.* **13**, 521 (1988)
5. P. Burgener and G. Légère, scang - instruction manual, Technical Service Laboratories, 1301 Fewster Drive, Mississauga, Ontario, Canada L4W 1A2
6. H. Hahn, *The Complete Guide to IBM PC AT Assembly Language*, Scott, Foresman and Company: Glenview, IL (1987)

APPENDIX C

Exposures

1)- GENERAL DESCRIPTION :

The exposures that were used to record the signals of mixtures of G-standards in graphite have been discussed in Chapter 2 of this thesis (cf. pages 62). The exposures that were used to record the signals of mixtures of sediment, graphite and AgCl have been discussed in Chapters 3, 4 and 5 (cf. pages 81,82,117,118,142,143 and 144). Again, for the sake of clarity and because these are an important aspect of this work, the piecemeal descriptions of exposures and data processing procedures are compiled in this appendix. The interested reader is also referred to appendix B for details on the spectrometers, since the two subjects are inseparable.

2)- EXPOSURES USED FOR MIXTURES OF G-STANDARDS :

The spectrometer that was used to record these signals was the Thermo Jarrell Ash ICAP 61. Its controller was designed for steady state signals, and it does not deal well with transient signals. The only option that allows consecutive time resolved off-line and on-line emission intensity measurements to be recorded is the SPECTRUM SHIFT option, in which a single integration time must be used for all the channels. Because the total number of exposures is fixed at 64, a compromise must be reached between the short integration times that are necessary to adequately resolve the short signals from shifts in the plasma's background emission, and the longer integration times that are needed to completely record the slower signals. Typically, either the fast signals of Cd, Hg and Pb appear as a single point in the time profiles, or the long signals of Fe, Mn and Ni are prematurely cut off. This dilemma is illustrated in Figures 3-a) and -b) of Chapter 2.

The data acquired with the Thermo Jarrell Ash ICAP 61 was stored in ASCII text files, which could later be imported in a spreadsheet. The use of a spreadsheet greatly lightened the burden of data analysis, and allowed interactive manipulation of the data. A straightforward background correction procedure was used for the SPEX g-standard data. A background estimate for each on-line point was calculated by linear interpolation between two bracketing off-line points, and directly subtracted. This procedure was implemented as a MACRO in Borland's QUATTRO spreadsheet program.

3)- EXPOSURES USED FOR SIMPLE MIXTURES OF SEDIMENT IN GRAPHITE :

Various exposures that took advantage of the greater flexibility of the operating program of the Légère system have been tried to record the signals from these burns. For example, exposures consisting of consecutive measurements at five wavelengths have been used. The wavelength interval between these positions varied, to cover different parts of the signal's wavelength profile. These exposures were of very little practical use, and they were soon abandoned.

After careful examination of the resulting signals for each kind of exposure and a critical assessment of their information content, only two types of exposures were kept :

1)- simple exposures consisting of consecutive measurements on the line and at a single off line wavelength

2)- consecutive wavelength scans across 32 wavelength positions, the wavelength interval between these positions was fixed at 0.002 nm for these exposures

the former has simplicity as its chief advantage, since it can be treated in exactly the same manner as the signals recorded with the ICAP 61. The main difference here, as discussed in Chapters 3 and 4 as well as Appendix B, is that the total number of measurements per exposure is considerably greater and that a different integration time can be assigned to each channel. The second type of exposure best highlights the spectral features of complicated signals, particularly when they appear over an equally complicated background.

The co-optimization of DSI and ICP parameters has already been reported to have permitted the adequate observation of the signals of elements of high and intermediate volatility with the simple exposures. The exposures consisting of consecutive wavelength scans were only used for diagnostic purposes during the optimization of the DSI and ICP parameters, until temporal resolution of the signals from their interferences was achieved.

The data processing program of the last section was slightly modified to automatically locate the start, peak and end times of the transient signals. The first derivative of the trace was used to locate the peak's maximum. The start and end times were then found by scanning outward from the peak's maximum. The criterion for deciding when the baseline had been reached was whether the value at that point had fallen within a 68%

confidence interval around the average of the next nine points in the scan's direction. Here, the baseline of the on-line trace was interpolated from the off-line trace by a cubic spline over the interval from the start to the end of the peak, and subtracted point by point. Numerical integration was found to provide the best compromise between accuracy and execution time.

4)- EXPOSURES USED FOR THE WORK WITH THERMOCHEMICAL ADDITIVES :

Initially, exposures consisting of 100 consecutive wavelength scans across 15 wavelength positions separated by 0.005 nm were used for this application (cf. Figure 2 of Chapter 5). However, it soon became apparent that half the exposure was spent recording inconsequential wavelength information. The wavelength resolution of the scans was thus increased, at the expense of their width and of the total duration of the exposure. Exposures consisting of 50 repeat scans across 32 spectrum shifter positions separated by 0.002 nm and centered on the middle of the channel's 0.256 nm span were thus implemented as in the last section.

The background intensity at the on-line position was calculated by fitting a fourth order polynomial across off-line positions on each side of the peak along the wavelength axis. The signal's baseline was then constructed by interpolation of each wavelength scan's polynomial at the on-line position, across the full duration of the exposure. The corrected signals were obtained by subtracting the interpolated baseline from the on-line trace, point by point. Finally, peak areas were calculated by numerical integration of the corrected signals.

The performance of the baseline correction procedure was evaluated using overlaid 3-D plots. Briefly, a background estimate was calculated for each position of the wavelength scans over the whole duration of the exposures. Axonometric plots of the raw signal and its background estimate were then generated and plotted in two colors. This was especially useful during the development of the baseline correction procedure, to determine the degree of the polynomial that best approximated the shape of the background at a given channel.

APPENDIX D

3-D plotting program

The sediment data was all acquired using the upgraded ATOMCOMP 97500, and its operating program stores data in 4 byte REAL format. Two programs were written in Pascal to process these files, a translation program and a 3-D program. The translation program essentially performed three tasks :

1)- read in 4 byte REAL data file
2)- determine number of spectrum shifter positions from file's header
3)- save data in comma delimited ASCII text file

the information from 2)- is used in 3)- to determine when to send a line feed to the text file. The text file thus appears as a series of lines with as many numbers per line as there were spectrum shifter positions in the exposure. The inclusion of commas between each number on a line is important because their presence greatly simplifies the *`File Import`* operation in QUATTRO.

The 3-D plotting program used a simple algorithm to display successive scans, whereby each scan was offset incrementally in the X and Y directions and plotted as a filled polygon. The plotting procedure started from the topmost polygon (i.e. highest index) and proceeded in decreasing order, so that the lower polygons obscured the part of the earlier ones that fell under them (see Figures 1 and 3 of chapter 5 for examples).

The program read in the 4 byte REAL files, checked the file's header to determine the number of spectrum shifter positions in the scans, and organized the data accordingly in an array. A procedure then scanned the array to determine the maximum and minimum intensities, and a scaling factor was calculated from their difference. A baseline was then calculated that was below the minimum intensity by an offset equal to one tenth of the scaling factor. The polygons were then constructed by connecting the points along a scan with lines, then going down both sides to the baseline and connecting with a straight line to close the polygon. The X and Y offsets were optimized empirically to maximize the depth of the plots without obscuring too much of the late features. The baseline correction procedure that was used to generate corrected profiles has already been described in chapter 5.

APPENDIX E

Direct sample insertion device

The direct sample insertion device (DSID) used in these studies was the stepper motor driven system designed by Sing and Salin [1,2], with minor modifications to accommodate the different torch box on the ICAP 61. Figure B-1 is a simplified diagram of the current prototype, a detailed description of its components, dimensions and operating principles will be found in ref. 1. The revised dimensions of the sample port, which connects to the torch box, are shown in Figure B-2. These dimensions fit both the ICAP 61 and Plasma Therm HFP2500D torch boxes.

The same design for a solenoid activated flow stopper was used to permit uninterrupted operation of the plasma, except that two solenoids were used : one to open the flow stopper and the other to shut it. It was found that the original design [1] had a tendency to stick, so that the flow stopper would remain closed upon insertion and the probe would be crushed against it. Figure B-3 is the schematic of the switching circuit for these solenoids.

A BIG STEPPER motion controller (CENTROID Corp., State College, PA) is used to control the stepper motor, as in the original design. This processor acts as a slave to the data acquisition system, to which it is interfaced via a RS-232 serial link. The BASIC control program is the same as the one developed by Sing [1], except that the various height parameters have been changed as the need arose.

The synchronization protocol first implemented by Sing (cf. lines 160 and 210 of the program in appendix D of ref. 1) was expanded. Input statements were used in the program to put out an alphabetic character at the serial port and wait for a numeric character to be returned. At the start of the program, and "A" was sent out with the expectation that a "1" would be returned. If everything went alright, the data acquisition program on the IBM controller and the BASIC program on the BIG STEPPER will both execute up to the next part where they need to talk again. Otherwise, the execution of both programs is halted and the program on the IBM PC puts out an error message. When the DSID is ready for insertion it puts out a "B" and waits for a "2" to be returned. Likewise, before triggering its data acquisition procedure the program on the IBM PC reads at the serial port expecting a "B". Upon receiving the "B", it puts out a "2" and proceeds to data acquisition and the program on the BIG STEPPER resumes execution when it receives the character "2". Finally, the BIG STEPPER sends a "C" after full retraction of the probe and it expects a "3" in return. This protocol prevents premature insertions and/or exposures, and aids in fault recovery.

REFERENCES

1)- R.L.A. Sing, Ph.D. Dissertation, McGill University, 1986

2)- E.D. Salin and R.L.A. Sing, *Anal. Chem.* **56**, 2596 (1984)

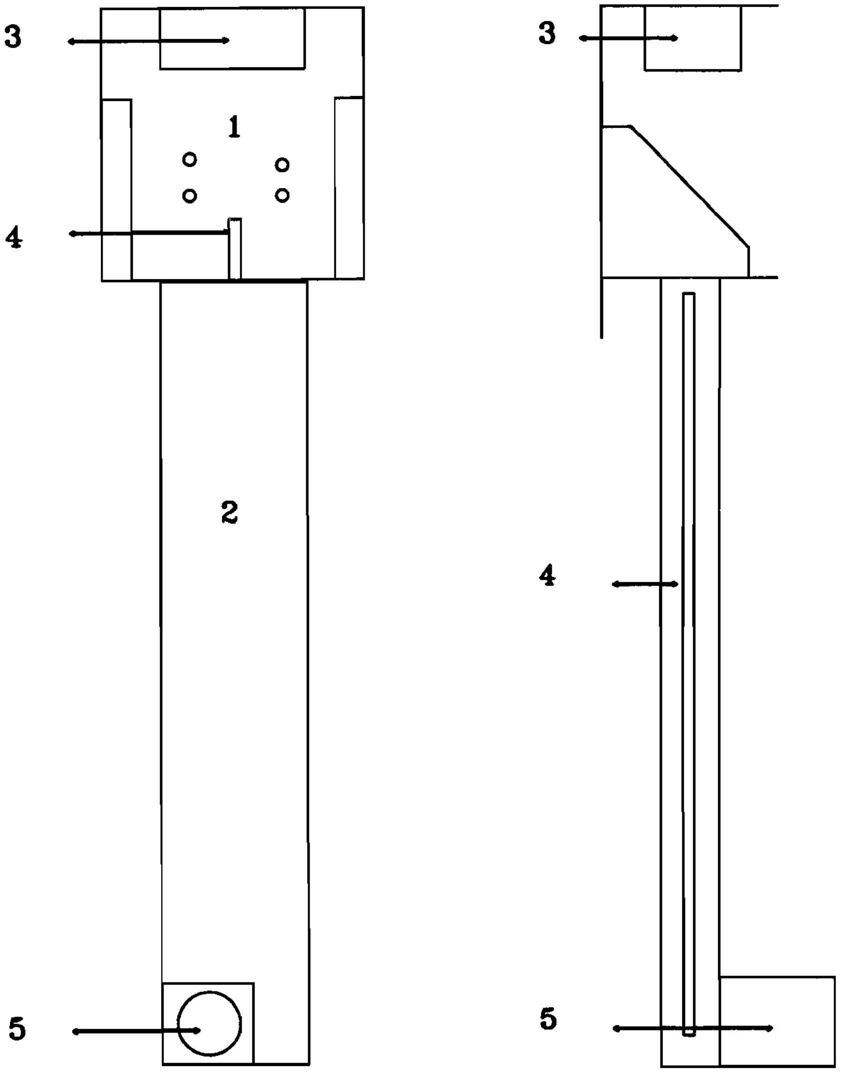


Figure B-1 : main components of stepper motor driven direct sample insertion device :

1)- sample port
2)- main body
3)- solenoid activated flow stopper
4)- shaft
5)- stepper motor

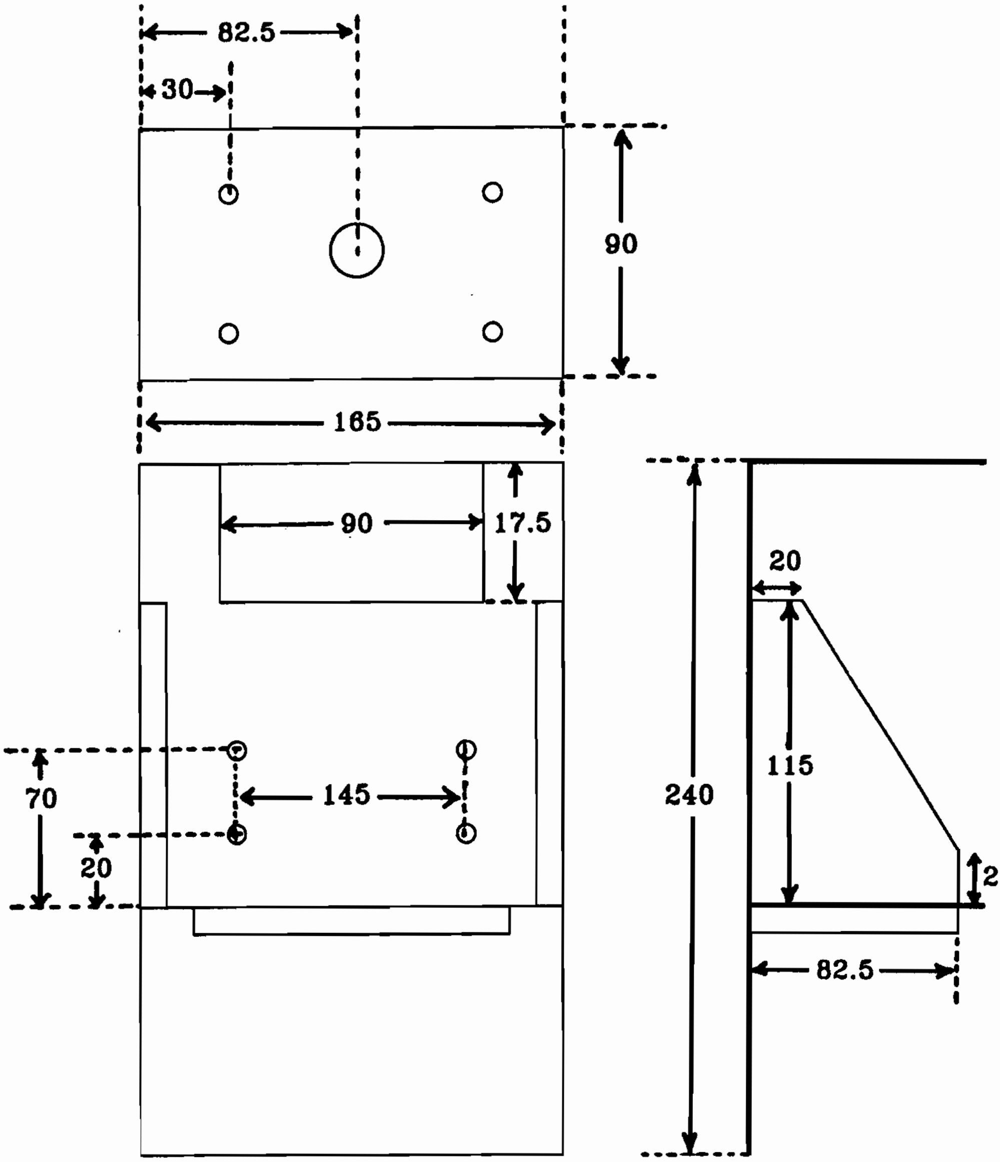


Figure B-2 : dimensions of sample port of direct sample insertion device, revised to fit on of Thermo Jarrell Ash ICAP 61 and Plasma Therm HFP2500D plasma boxes

dimensions are in mm

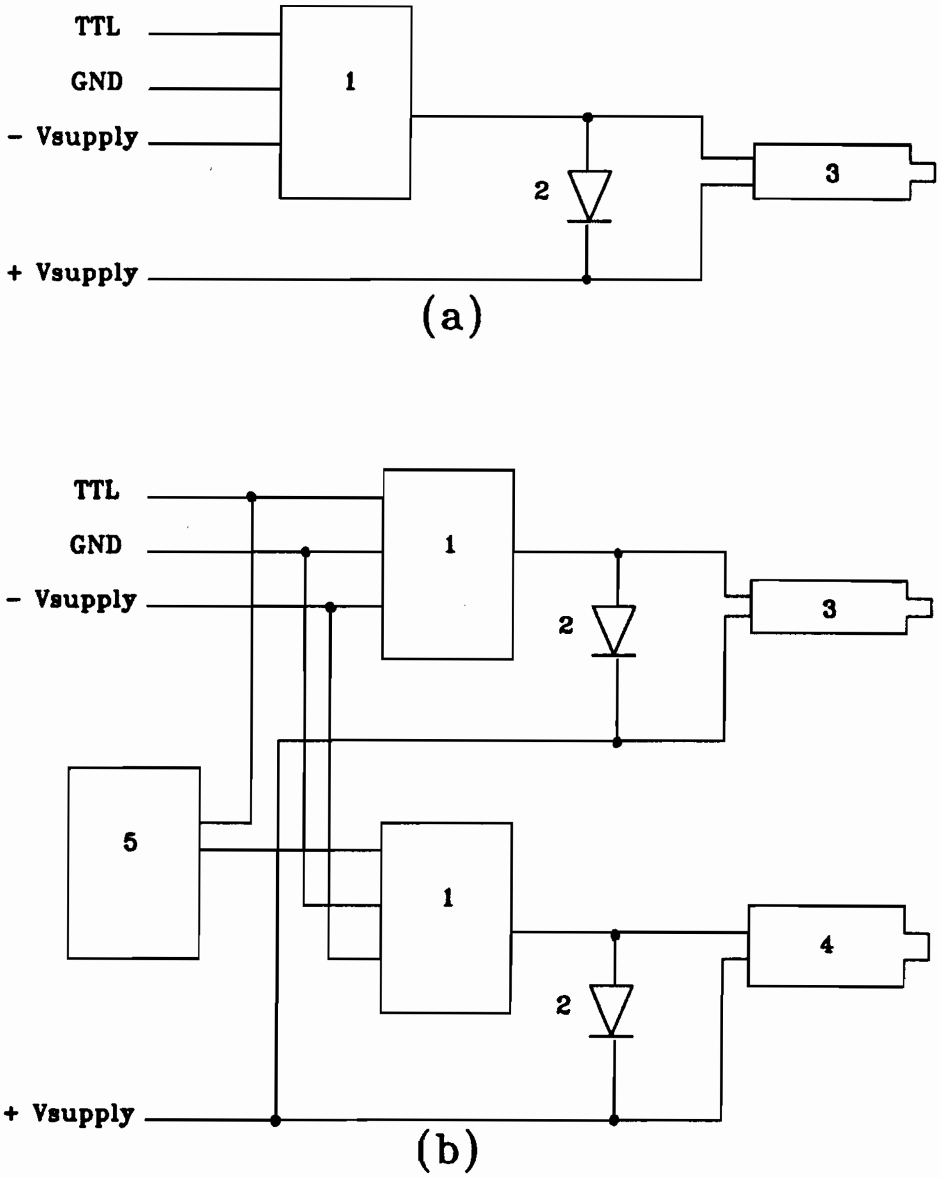


Figure B-3 : schematic of the circuit used to control solenoids on flow stopper of direct sample insertion device

a)- original design by Sing [1]

b)- revised design

list of parts :

1)- ODC5 Potter & Brumfield solid state relay
2)- 1N4004, general purpose rectifier
3)- TP6 x 12 solenoid (pull type, 12V)
4)- TP6 x 24 solenoid (pull type, 24V)
5)- 74LS04, Hex inverter (active pull up)

APPENDIX F

DSI torch

The DSI torches used for this work were composed of two concentric quartz tubes, with the characteristic tulip shape expansion at the tip of the inner tube. This torch is different from conventional ICP torches only by the absence of a central injector tube. This design has been used consistently by Salin's group [1,2,3,4], and is only different here by the dimensions of the tulip shape expansion :

Outer tube (i.d.)		18 mm
Inner tube	(i.d.)	(o.d.)
above the tulip shape expansion	12 mm	14 mm
below the tulip shape expansion	10 mm	12 mm
Gas port (i.d.)		4 mm
Length of the outer tube above the tulip shape expansion		26 mm
Length of the inner tube above the tulip shape expansion		24 mm

It was found that a longer tulip shape expansion and a greater length of outer tube above the tulip shape expansion resulted in a steadier plasma that could better withstand the intrusion of the direct sample insertion probes. A Teflon sleeve is used to align the base of the torch with the port on the DSID's top plate. In an earlier prototype, the torch connected directly with the top plate and often the base of the torch was cracked because of stress resulting from slight misalignments.

REFERENCES

1)- E.D. Salin and M.M. Habib, *Anal. Chem.* **56**, 1186 (1984)
2)- M.M. Habib and E.D. Salin, *Anal. Chem.* **57**, 2055 (1985)
3)- E.D. Salin and R.L.A. Sing, *Anal. Chem.* **56**, 2596 (1984)
4)- C.V. Monasterios, A.M. Jones and E.D. Salin, *Anal. Chem.* **58**, 780 (1986)