



NRC Publications Archive Archives des publications du CNRC

Iridium as a permanent modifier for determination of cadmium and lead in sediment and biological samples by furnace atomization plasma emission spectrometry

Grinberg, P.; Campos, R. C.; Sturgeon, R.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1039/b203030f>

Journal of Analytical Atomic Spectrometry, 17, 7, pp. 693-698, 2002

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=e15dbb2b-1288-4a22-b987-e577d346c42c>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=e15dbb2b-1288-4a22-b987-e577d346c42c>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.



Iridium as a permanent modifier for determination of cadmium and lead in sediment and biological samples by furnace atomization plasma emission spectrometry

Patricia Grinberg,^a Reinaldo C. Campos^b and Ralph E. Sturgeon^{*a}

^a*Institute for National Measurements Standards, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. E-mail: ralph.sturgeon@nrc.ca*

^b*Department of Chemistry, Pontificia Universidade Católica do Rio de Janeiro, Rua Marquês de São Vicente, 225, 22453-900 Rio de Janeiro-RJ, Brazil*

Received 26th March 2002, Accepted 29th May 2002

First published as an Advance Article on the web 18th June 2002

The use of iridium as a permanent modifier for the determination of lead and cadmium in marine sediment and biological tissues by furnace atomization plasma emission spectrometry (FAPES) was evaluated. The Ir coating procedure, atomization conditions and FAPES parameters were optimized for best analytical response and minimum background signal. Good precision (less than 3% RSD) can be achieved with the proposed method. Certified Reference Materials from the National Research Council of Canada were analyzed to verify the accuracy of this technique. Matrix interference was compensated for by the use of standard additions calibration and good agreement was achieved between found and certified values. Detection limits of 3.8 ng g⁻¹ for Pb and 4.0 ng g⁻¹ for Cd in MESS-3 and PACS-2 marine sediment and 4.1 ng g⁻¹ for Pb and 2.2 ng g⁻¹ for Cd in DOLT-2 and TORT-2 biological tissues were obtained.

Introduction

Furnace atomization plasma emission spectrometry (FAPES), based on a capacitatively coupled radiofrequency He plasma formed between a graphite tube and a central electrode, has been extensively studied since its inception in 1989^{1,2} and great effort has been made to characterize the FAPES technique through analytical application as well as plasma diagnostics. With this technique, an atmospheric pressure plasma is created within the volume of the graphite tube and uniformly fills it over the length of a central antenna electrode. Analyte atoms, generated during the heating program, are excited in this plasma and emit optical radiation.

The analytical advantages of the graphite furnace are intimately coupled with those of the radiofrequency (rf) He plasma, *i.e.*, the atomizer allows *in situ* sample pre-treatment and the plasma provides excellent atomic and molecular emission sensitivities (due to the high plasma excitation temperatures of about 3500 K), generating detection limits comparable to those achieved by electrothermal atomic absorption spectrometry (ETAAS).²⁻⁶

The analytical performance of the FAPES technique is influenced by the sample matrix, as this alters the plasma working conditions such that analyte response suffers interference effects,⁵ especially from easily ionized elements^{3,7} that can change the plasma electron density and temperature.

In an effort to overcome this problem, Sturgeon *et al.*⁵ reported the use of platform atomization and palladium modification techniques in conjunction with FAPES. The detection limit, sensitivity and precision achieved for volatile elements were improved and the removal of matrix species was possible prior to the atomization step. However, the usual practice of introducing the chemical modifier prior to each sample was problematic, as vaporization of relatively large masses of modifier material tends to quench the plasma.

In the past decade, increasing attention has been given to the use of permanent modifiers,⁸ such as iridium, for application in ETAAS. In such case, the modifier is introduced prior to the analysis by thermodeposition, electrodeposition or sputtering

processes⁹⁻¹¹ and persists in the atomizer for numerous atomization cycles. For elements such as Pb, the modifying capability of Ir may last beyond 1100 firing cycles, even in the presence of complex matrices such as urine and blood, if the proper coating temperature program is used.¹² The permanent modifier has the advantage of not only decreasing the analysis time and cost because the need to introduce the modifier before each analysis is eliminated, but any volatile impurities can be removed during the pre-treatment of the modifier in the furnace, leading to minimization of the blank.

The utilization of Ir as a permanent modifier in conjunction with the FAPES technique should overcome the drawbacks of conventionally introduced modifiers, expanding application of this technique. In this study, the performance of a permanent Ir modifier was examined for use in the determination of lead and cadmium in marine sediment Certified Reference Materials PACS-2 and MESS-3, as well as biological tissue DOLT-2 and TORT-2, by FAPES.

Experimental

Instrumentation

The FAPES system, described in detail previously,^{2,7,13} is based on a 40.68 MHz rf He plasma supported inside a Perkin-Elmer Model HGA-2200 graphite furnace (Norwalk, CT). A Model RF10L 40.68 MHz rf generator (Advanced Energy Ind., Fort Collins, CO) provided 20–200 W of rf power to a 1 mm diameter pyrolytic graphite coated electrode which was centred along the axis of the graphite tube. The rf power supply was connected through an AM-5L impedance matching network.

A 0.5 m Varian monochromator (Springvale, Australia) equipped with a Hamamatsu R446 PMT operated at –550 V was used for wavelength isolation and intensity measurement. Data were collected and manipulated by an IBM 486 PC using in-house software written in Turbo Pascal version 4.0 (Borland International, Scotts Valley, CA).

The furnace was heated by a Perkin-Elmer HGA-2200 power supply. The temperature feedback controller for this unit was

interfaced to a remote photodiode, which monitored the temperature of the furnace, thereby providing “maximum power” heating capability.

Hollow cathode lamps (Intensitron, Perkin-Elmer) were used as line sources. Pyrolytic graphite coated tubes (Perkin-Elmer, Norwalk, CT, USA) were used throughout.

An Ar external sheath gas was maintained at a flow-rate of 1 l min⁻¹ and a He internal plasma gas was set at flow-rates of between 20 and 500 ml min⁻¹.

Sample preparation was achieved by mixed acid digestion in Teflon pressure vessels placed in a CEM model MDS 2100 (Matthews, NC) microwave digestion system.

Reagents

Stock solutions (1000 mg l⁻¹) were prepared by dissolution of the high-purity metals. Working standards were prepared by serial dilutions of the 1000 mg l⁻¹ stock solutions using high-purity, de-ionized, distilled water (DDW) acidified to 1% v/v with sub-boiling, quartz distilled HNO₃. Industrial grade He and Ar (Praxair Products Inc., Mississauga, ON) were used throughout.

Ir was deposited on the tube wall using a 5000 mg l⁻¹ IrCl₃ solution prepared by dilution of a 10 000 mg l⁻¹ IrCl₃ stock in 20% HCl solution (Alfa Aesar, Ward Hill, MA).

Samples

The following Certified Reference Materials were used for verifying the accuracy of the proposed method: NRCC (National Research Council of Canada) DOLT-2 dogfish liver, NRCC TORT-2 lobster hepatopancreas and NRCC MESS-3 and PACS-2 marine sediments.

Sample preparation

Biological materials. A nominal 0.25 g sample was accurately weighed into a Teflon digestion vessel (CEM Type) and 7 ml of HNO₃ were added. The vessel was capped and the sample was digested using microwave heating at a pressure of 120 psi for 30 min. After cooling, 200 µl H₂O₂ (30%) was added, the samples were recapped and heated again using the same microwave program. The digested material was then cooled and diluted to 25 ml with deionized water.

Sediments. A nominal 0.25 g sample was accurately weighed into a Teflon digestion vessel (CEM Type) and 3 ml HNO₃, 3 ml HF and 1 ml HClO₄ were added. The vessel was capped and the sample was digested using microwave heating at a pressure of 120 psi for 25 min. After cooling, the cap was removed and the open vessel was heated on a hotplate overnight in a class 10 fume hood until dry. 1 ml HNO₃ and 5 ml deionized water were then added to the vessel, which was gently heated to dissolve the residue. The digested material was then cooled and diluted to 50 ml with deionized water. Blanks were also prepared in conjunction with both digestion procedures by subjecting all reagents to identical manipulations described for the samples.

Procedure

Working wavelengths were set using Pb and Cd hollow cathode lamps. A nominal spectral bandwidth of 0.06 nm was used for all intensity measurements.

After the conditioning of a new tube and electrode, the Ir coating was achieved thermally by pipetting 20 µl of the 5000 mg l⁻¹ Ir solution and subjecting the tube to the temperature program given in Table 1.¹² This procedure was repeated 12 times.

All temperatures cited are those read from the power supply

Table 1 Temperature program for the permanent Ir modifier

Step	Temp/°C	Ramp/s	Hold/s	He/ml min ⁻¹
1	90	5	5	300
2	150	20	10	300
3	1000	99	5	300
4	20	5	10	100
5	2300	1	10	100
6	2500	5	2	100
7	20	2	15	100

and may not accurately reflect the real temperature of the tube surface.

For the initial data, sample volumes of 10 µl were manually introduced into the graphite furnace using an adjustable pipette and the graphite furnace temperature program was initiated. The samples were first dried at 120 °C for 30 s and then charred at 500 °C. The char step lasted for 40 s. The rf power was applied 20 s before the atomization step, during which the He plasma spontaneously ignited. After this period, the sample was atomized using the maximum power heating mode and the analyte emission signal recorded. The rf power was then turned off, the furnace permitted to cool and the sequence repeated.

Blank signals, recorded for both analytes, were obtained by atomizing 10 µl of DDW containing 1% v/v HNO₃.

Background correction with this system was limited to sequential measurement of a solvent blank with subtractions of this signal from the analyte signal. It should be noted that any small blank peak recorded might not be due to contamination but could result from continuum emission from molecular species (*i.e.*, CO, N₂ and OH) or from the plasma itself.¹⁴

Results and discussion

Optimization of coating procedures

The utilization of a conventional Pd modifier has already been studied with the FAPES system⁵ and showed beneficial effects, especially for volatile elements such as Pb and Cd. Analyte emission signals were temporally delayed and use of higher pyrolysis temperatures was possible without losing the analytes prior to the atomization step. However, there are some drawbacks to the use of a conventional modifier, as noted earlier, and the use of Ir as a permanent modifier should prove of benefit.

In order to optimize the Ir coating process, two factors were investigated: the coating of the furnace wall and the coating of the graphite electrode. It was noted that when the graphite electrode was not present during the coating procedure, poor signal reproducibility was achieved. By coating both the tube wall and the graphite electrode, the signal intensity (peak area and peak height) was higher than when only the electrode was coated and reproducibility was improved.

Analyte solutions are initially deposited on the furnace wall; during the pyrolysis and atomization cycles, analyte may be volatilized and condense on the cooler center electrode.¹⁵ Subsequently, convection and radiation heating of this surface by the hotter tube wall serves to reatomize the analyte.¹⁶ Both the graphite tube wall and the center electrode thus play an important role during both the pyrolysis and atomization steps. All subsequent studies were therefore performed following coating of both furnace wall and center electrode. The Ir coated tube/electrode system lifetime was shorter than that of the Ir coated tube alone, where more than 1100 firing cycles could be used with the same tube.¹² It was verified that the lifetime of the tube/electrode system is governed by the erosion of the electrode that occurs preferentially near the injection hole. The erosion rate of the thin Ir coating layer of the center electrode during the atomization cycle also dominates the lifetime of the tube/electrode system, and further affects reproducibility. As

noted earlier, the electrode is centred along the axis of the graphite tube and is supported at only one end. After approximately 300 firing cycles, erosion thins the electrode opposite the injection hole, making it so fragile that it must be replaced.

Optimization of the FAPES system

The most sensitive lines, *i.e.*, the resonance emission lines at 283.3 nm and 228.8 nm for Pb and Cd, respectively, were selected for evaluation of the analytical utility of the permanent modifier. 50 W rf forward power was used for optimization studies, unless stated otherwise. Typical emission transients arising from both elements are illustrated in Fig. 1, which shows the dramatic effect of the permanent modifier in delaying the release of analyte into the plasma. As the heating rate of the tube wall was approximately 1750 K s^{-1} , the appearance time for Cd, for example, was delayed by nearly 500 K relative to the system containing no Ir modifier. Further, the peak height and integrated response were enhanced, as elaborated below.

Optimum furnace conditions

The pyrolysis and atomization conditions were varied in order to determine the temperatures for optimum analytical response and minimum background signal. Results are summarized in Fig. 2. As both the peak area and peak height response showed the same trend, Fig. 2 illustrates only peak area measurements.

It appears from the data in Fig. 2 that the optimum pyrolysis temperatures are $1000\text{ }^{\circ}\text{C}$ for Pb and $900\text{ }^{\circ}\text{C}$ for Cd. However, when temperatures higher than $800\text{ }^{\circ}\text{C}$ were used for Pb, the emission transient was broadened, with the result that the optimum pyrolysis temperature for Pb utilized in subsequent experiments was $800\text{ }^{\circ}\text{C}$. This was likely to be a consequence of redistribution of the lead between the tube wall and center electrode at pyrolysis temperatures close to its appearance temperature, resulting in secondary (delayed) release from the electrode during atomization and a broadening of the signal.

The effect of pyrolysis time was also studied. It was necessary that this stage be of at least 20 s duration in order to

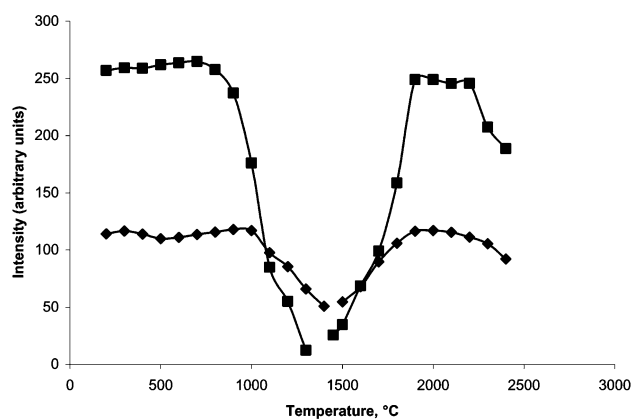


Fig. 2 Pyrolysis and atomization temperature curves for (◆) 1 ng Pb and (■) 0.5 ng Cd using the Ir-treated tube. Atomization temperatures in the pyrolysis experiment: $2000\text{ }^{\circ}\text{C}$ with m.p. heating; pyrolysis temperature in the atomization experiment: $250\text{ }^{\circ}\text{C}$.

spontaneously ignite and stabilize the He plasma before the atomization stage. For both elements, the background decreased for pyrolysis times longer than 40 s. The source of the background was likely the presence of CO molecular bands in the region of both wavelengths.¹³ This molecular emission arises due to ingress of ambient atmosphere, the presence of impurities in the He gas or, more likely, the formation of CO by the reaction between HNO_3 and/or H_2O present in the sample with the carbon of the graphite tube. A pyrolysis time of 40 s was thus used in all subsequent studies.

With the impedance matching network connected to the rf power supply and operated in the manual mode, reflected power can be tuned to less than 1 W when the furnace is at room temperature. It is known that when the furnace is heated above $2500\text{ }^{\circ}\text{C}$, reflected power levels increase, reducing the efficiency of power coupling into the plasma. The loss in forward power, combined with decreased analyte residence times at high temperature, is likely to contribute to the decreased analytical response at these higher temperatures. The optimum atomization temperature was found to be $1900\text{ }^{\circ}\text{C}$ for both elements.

The use of maximum power heating was also evaluated and resulted in the expected narrower, more intense emission peaks for both elements.

Optimum conditions for the furnace program are summarized in Table 2.

Plasma gas flow

The influence of He plasma gas flow rate through the furnace on analyte response was examined; results are summarized in Fig. 3 and typical emission transients for Pb and Cd, along with their associated blank signals, are shown in Fig. 4 at two extreme He flow rates.

For Pb, enhancements in intensity for both peak area and peak height arise as the plasma gas flow rate is decreased from 500 ml min^{-1} to approximately 100 ml min^{-1} . A stable plasma could be maintained only at flow rates greater than 40 ml min^{-1} , likely to be because of ingress of both the external sheath gas

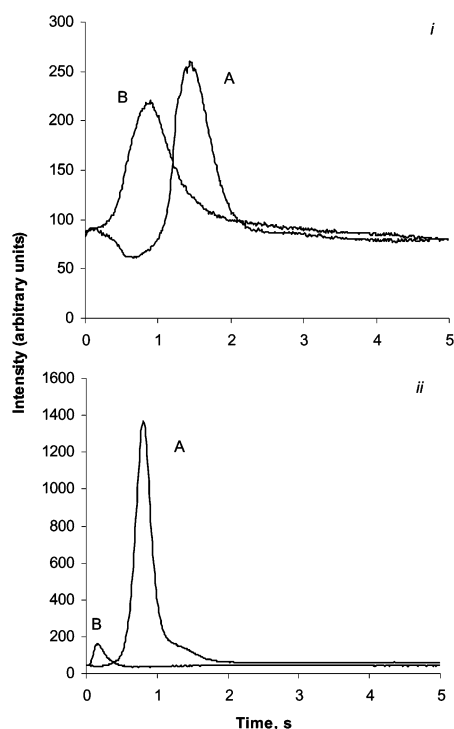


Fig. 1 Temporal emission profiles of Pb and Cd in the presence and absence of permanent Ir modifier. (i) Atomization of 1 ng Pb in the presence (A) and absence (B) of Ir coating; (ii) atomization of 0.5 ng Cd in the presence (A) and absence (B) of Ir coating.

Table 2 Optimum conditions for the furnace

	Pb	Cd
Pyrolysis temperature/ $^{\circ}\text{C}$	800	900
Pyrolysis time/s	40	40
Atomization temperature/ $^{\circ}\text{C}$	1900	1900
Atomization time/s	5	5
Maximum power	Yes	Yes
He plasma gas/ ml min^{-1}	100	100

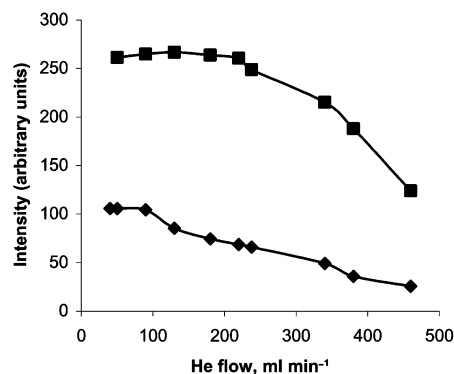


Fig. 3 Effect of He plasma gas flow rate on integrated response for (◆) 1 ng Pb and (■) 0.5 ng Cd using the Ir-treated tube.

(Ar) and ambient atmosphere into the tube *via* the sample dosing hole^{17,18} at lower flow rates, leading to plasma quenching. At high flow rates the analyte residence time is reduced, leading to a loss in response.

For Cd, intensities for both peak area and height are constant for He flow rates below 220 ml min⁻¹. It was also noted that the background intensities were similar for both He flow rates but the Cd transients exhibited irregular peaks for flow rates higher than 130 ml min⁻¹. Thus, a flow rate of 50 ml min⁻¹ was selected for all further measurements for both elements.

Forward power

Fig. 5 illustrates the effect of forward rf power on the response for Pb and Cd.

For Cd, as forward rf plasma power increases, there is a corresponding increase in both peak height and area analyte emission intensity. Several factors may account for this: an increase in forward power results in a slight increase in the excitation temperature of the plasma and an enhancement in the volume of the plasma excitation region. Additionally, the

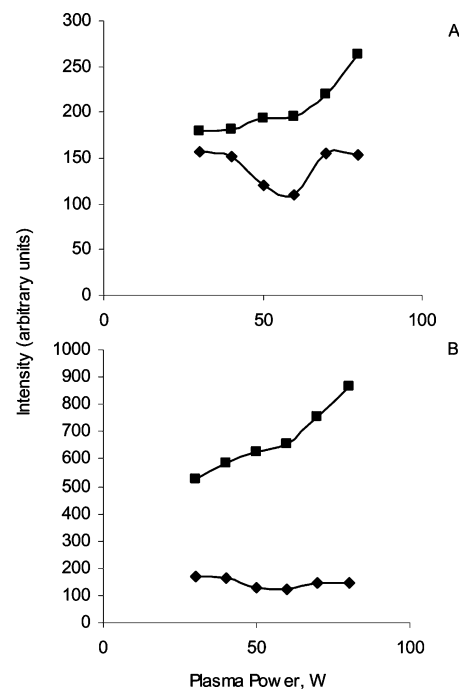


Fig. 5 Optimization of the forward He plasma power for (◆) 1 ng Pb and (■) 0.5 ng Cd using the Ir-treated tube. A: peak area measurements; B: peak height measurements.

electron density and its energy distribution function within the plasma are increased, enhancing excitation rates.¹³

For Pb, a different pattern is evident; a dip in response occurs at plasma powers of 50 and 60 W. The reason for this is not clear at this time, but may be related to some change in the physical characteristics of the plasma, which alter its volume and, consequently, the residence time of Pb. The same effect is not evident for Cd, possibly because of its earlier (lower temperature) release from the surface.

When using forward plasma power higher than 70 W, arcs and filaments start to appear, making the plasma very unstable.

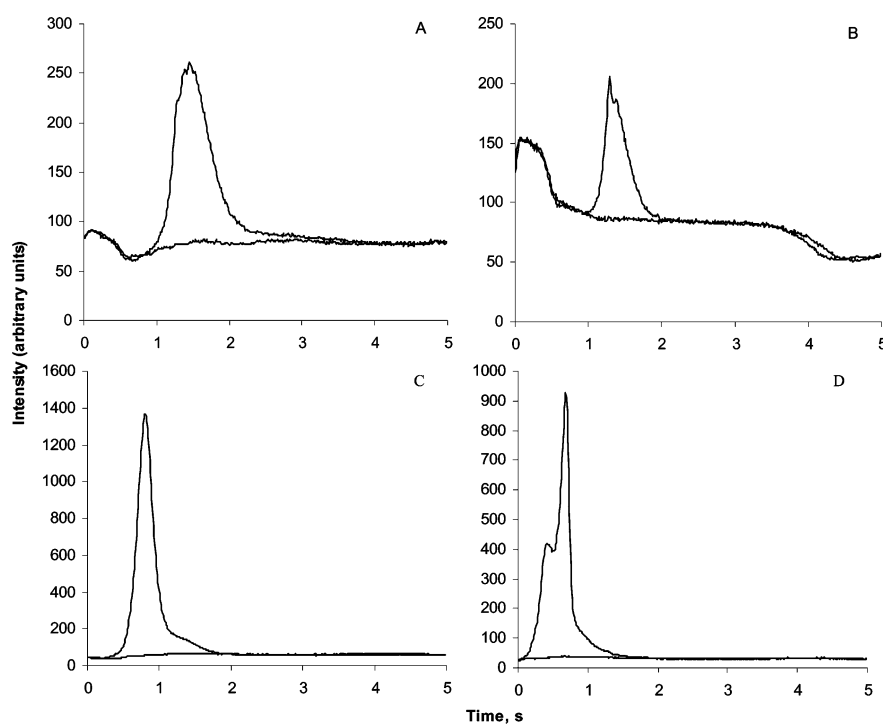


Fig. 4 Emission transients for Cd and Pb at different He flow rates: A: 1 ng Pb at 50 ml min⁻¹; B: 1 ng Pb at 300 ml min⁻¹; C: 1 ng Cd at 50 ml min⁻¹; D: 1 ng Cd at 300 ml min⁻¹. The lower trace in each panel displays the corresponding background signal.

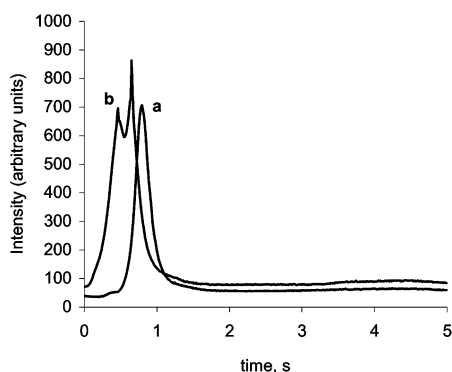


Fig. 6 Temporal emission profiles for atomization of 0.5 ng Cd at different plasma power: (a) 60 W; (b) 80 W.

Additionally, as the rf power is increased, a broadening of the analyte emission profiles and a small shift in the appearance time of the emission transients to earlier times occurs, as exemplified by Cd in Fig. 6. This is most likely a consequence of the increased temperatures of both the tube wall and center electrode, which accompany forward plasma power increases.

Calibration

Analytical figures of merit were obtained under optimum conditions and are summarized in Table 3. Precision of replicate measurements was calculated for each day and determined by the repeatability of manual injection of 10 consecutive samples containing analyte concentrations approximately 100 times higher than the limit of detection (LOD). The results presented reflect a pool of data covering a period of 3 months. Peak area data provide, for both elements, more precise results. This same characteristic is also observed in ETAAS.¹⁹

Background equivalent concentrations (BEC) for peak height measurements were calculated at the time corresponding to the peak of the analyte signal.

Limits of detection were calculated using the 3σ , IUPAC criterion, where σ_b is the estimate of the standard deviation of at least 10 repeated measurements of the blank. The data presented in Table 3 were obtained using two different approaches: integrating the signal using a constant time window selected to best fit the entire emission transient of

each element based on the highest calibration solution used, and by varying the integration window in accordance with the concentration, *i.e.*, the interval is the best fit for each concentration and was typically narrowed as the analyte concentration decreased. The LOD reported here is appropriate for a 1% v/v HNO₃ solution of each analyte. The estimated procedural LODs for the determination of Cd and Pb in biological samples are 4.1 ng g⁻¹ for Pb and 2.2 ng g⁻¹ for Cd and in sediment samples are 3.8 ng g⁻¹ for Pb and 4.0 ng g⁻¹ for Cd.

From Table 3, it is evident, especially for Pb, that when the best fit interval is used for each concentration, superior peak area results can be achieved as a consequence of lower overall extraneous noise being integrated over the duration of the signal.

Peak height LODs are generally superior to those derived from peak area measurements as is frequently the case in ETAAS.²⁰ An approximately 10-fold enhancement in performance was achieved when using Ir compared with results using platform atomization and Pd modifier.⁵ Additionally, an improvement of three orders of magnitude in the procedural LOD was achieved for the determination of Pb in sediment samples compared to results with a similar sediment sample (BCSS-1) and for sample atomization from the tube wall without a modifier.⁷

Analytical results

The accuracy of the proposed methodology was verified by the analysis of Certified Reference Materials of biological samples and marine sediments. Results are summarized in Table 4. Digested samples were prepared prior to analysis using the following dilutions: 20-fold for determination of Pb in MESS-3 and for determination of Cd in biological materials and PACS-2; two-fold for determination of Pb in biological materials and determination of Cd in MESS-3 and 100-fold prior to analysis of PACS-2 for determination of Pb.

The method of standard additions with peak area quantitation was used for calibration. Good agreement between found and certified values is evident for all samples. Attempts to use a simple calibration curve prepared from external standards were unsuccessful for quantitation of real samples due to changes in response as a consequence of the covolatilized matrix. For determination of Pb, an enhancement of the signal (*ca.* 15% for biological materials, 20% for MESS-3 and 60% for PACS-2) was observed in the presence of both matrices whereas for Cd, the signal was suppressed (*ca.* 55% for biological materials, 20% for MESS-3 and 60% for PACS-2).

For the determination of Pb in biological materials and Cd in marine sediment (MESS-3), minimal (two-fold) dilution of the sample was used due to the low concentrations of these analytes, leading to relatively large amounts of easily ionizable elements (EIEs; *e.g.*, Ca, Na, Mg, K) entering the plasma. Earlier studies^{6,21-22} showed that the vaporization of large amounts of EIEs into the plasma changes plasma impedance, resulting in more reflected power and therefore less power available for excitation. This impacts several factors, such as analyte residence time, atomization efficiency, degree of

Table 3 Figures of merit

	Pb		Cd	
	Peak Height	Peak Area	Peak Height	Peak Area
Precision/% RSD	2.2	1.9	2.3	2.2
BEC/ng ml ⁻¹	8	—	4	—
Limit of detection/pg (Varied integration window)	0.15	0.43	0.07	0.08
Limit of detection/pg (Fixed window)	0.16	0.58	0.07	0.08

Table 4 Analytical results

Sample	Pb/mg kg ⁻¹		Cd/mg kg ⁻¹	
	Certified value ^a	Determined ^b	Certified value ^a	Determined ^b
DOLT-2	0.22 ± 0.02	0.29 ± 0.10	20.8 ± 0.5	19.9 ± 0.7
TORT- 2	0.35 ± 0.13	0.48 ± 0.13	26.7 ± 0.6	26.6 ± 0.5
MESS-3	21.1 ± 0.7	20.88 ± 1.3	0.24 ± 0.01	0.31 ± 0.09
PACS-2	183 ± 8	185 ± 8	2.11 ± 0.15	2.10 ± 0.31

^aUncertainty reflects 95% confidence interval. ^bMean and sample standard deviation ($n = 3$).

ionization and excitation efficiency that are intimately related to the analyte response.

The presence of each major component of the matrix alone, at a concentration of 5000 mg l^{-1} , did not change the reflected power characteristics of the plasma, but when synthetic matrices having the same inorganic composition as both samples were used, synergistic effects were noted which lead to significant changes in the sensitivity.

For Pb, in the presence of both sample matrices, the appearance time was similar to that for standards but the peak profile was slightly broadened; for Cd the appearance time was somewhat later than that for standards.

Double peaks appeared in the Cd signal transients arising from sediment sample matrices. Double peaks frequently occur in FAPES as a result of re-distribution of analyte from the wall to the cooler center electrode.^{3,13,15,23} However, it was verified that only the first such peak responded to changes in analyte concentration, whereas the second peak remained constant. The identity of the second peak was never verified, but it likely arises as a consequence of the presence of matrix components rather than second surface vaporization phenomena²³ involving analyte being released from the cooler center electrode. This effect is less likely to occur in the presence of a sample matrix because the latter increases the appearance time (cf. Fig 1), which minimizes the likelihood of condensation and release from the center electrode.

Conclusion

The utilization of iridium as a permanent modifier affords several advantages to the FAPES technique for the analysis of complex samples which cannot be realized with conventional modifiers. Since the modifier does not need to be introduced prior to each sample and persists in the atomizer for numerous atomization cycles, the usual drawback of the modifier is eliminated. Additionally, large masses of modifier are not introduced into the plasma, contributing to the suppression of response.

The coating procedure plays an important role in the performance of the method and best results were achieved when both the graphite tube wall and the center electrode were coated. Synergistic effects from easily ionizable elements were verified, leading to a significant change in the response which could be overcome with the use of the method of standard additions. Moreover, good agreement was also obtained between determined and certified values in the analysis of complex digests arising from marine sediments and biological tissues.

Acknowledgement

P.G. thanks the Brazilian National Research Council for financial support while in Canada and S. Willie for his help in preparing the reference material samples for analysis.

References

- 1 C. D. Liang and M. W. Blades, *Spectrochim. Acta, Part B*, 1989, **44**, 1059.
- 2 R. E. Sturgeon, S. N. Willie, V. T. Luong, S. S. Berman and J. G. Dunn, *J. Anal. At. Spectrom.*, 1989, **4**, 669.
- 3 D. L. Smith, D. C. Liang, D. Steel and M. W. Blades, *Spectrochim. Acta, Part B*, 1990, **45**, 493.
- 4 P. R. Banks, D. C. Liang and M. W. Blades, *Spectroscopy*, 1992, **7**, 36.
- 5 R. E. Sturgeon, S. N. Willie, V. T. Luong and S. S. Berman, *J. Anal. At. Spectrom.*, 1991, **6**, 19.
- 6 R. E. Sturgeon, V. T. Luong, S. N. Willie and R. K. Marcus, *Spectrochim. Acta, Part B*, 1993, **48**, 893.
- 7 R. E. Sturgeon, S. N. Willie, V. T. Luong and S. S. Berman, *J. Anal. At. Spectrom.*, 1990, **5**, 635.
- 8 D. L. Tsalev, V. I. Slaveykova, L. Lampugnani, A. D'Ulivo and R. Georgieva, *Spectrochim. Acta, Part B*, 2000, **55**, 473.
- 9 E. Bulska, K. Liebert-Ilkowska and A. Hulanicki, *Spectrochim. Acta, Part B*, 1998, **13**, 1057.
- 10 E. Bulska and W. Jedral, *J. Anal. At. Spectrom.*, 1995, **10**, 49.
- 11 C. J. Rademeyer, B. Radziuk, N. Romanova, N. P. Skaugset, A. Skogstad and Y. Thomassen, *J. Anal. At. Spectrom.*, 1995, **10**, 739.
- 12 P. Grinberg and R. C. Campos, *Spectrochim. Acta, Part B*, 2001, **56**, 1831.
- 13 R. E. Sturgeon, S. N. Willie, V. T. Luong and S. S. Berman, *Anal. Chem.*, 1990, **62**, 2370.
- 14 R. E. Sturgeon and H. Falk, *Spectrochim. Acta, Part B*, 1988, **43**, 421.
- 15 S. Imai and R. E. Sturgeon, *J. Anal. At. Spectrom.*, 1994, **9**, 493.
- 16 S. Imai, R. E. Sturgeon and S. N. Willie, *J. Anal. At. Spectrom.*, 1994, **9**, 759.
- 17 R. E. Sturgeon and R. Guevremont, *J. Anal. At. Spectrom.*, 1998, **13**, 229.
- 18 F. Sun and R. E. Sturgeon, *Spectrochim. Acta, Part B*, 1999, **54**, 2121.
- 19 J. Sneddon, in *Sample Introduction in Atomic Spectroscopy*, ed. J. Sneddon, Elsevier, Amsterdam, 1990, p. I.
- 20 R. E. Sturgeon, S. N. Willie and V. T. Luong, *Appl. Spectrosc.*, 1991, **45**, 1413.
- 21 S. Imai and R. E. Sturgeon, *J. Anal. At. Spectrom.*, 1994, **9**, 765.
- 22 V. Pavski, R. E. Sturgeon and C. L. Chakrabarti, *J. Anal. At. Spectrom.*, 1997, **12**, 709.
- 23 T. D. Hettipathirana and M. W. Blades, *J. Anal. At. Spectrom.*, 1992, **7**, 1039.