Slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry for steelmaking flue dust analysis

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Abstract

A commercial atomic absorption graphite furnace (AAGF), with a self-made adapter and valve system, was used as a slurry sampling cell for electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). The system was applied to the determination of As, Sn, Sb, Se, Te, Bi, Cd, V, Ti and Mo in steelmaking flue dusts. Experimental conditions with respect to ETV and ICP-MS operating parameters were optimized. Compared to aqueous solutions, slurry samples were found to present better analyte transport. Microgram amounts of Rh were used to reduce the difference in analyte response in sensitivity for aqueous solutions of the tested analytes. No such increasing effect was observed for slurry samples and aqueous standards. An added quantity of Rh acting as modifier/carrier resulted in an increase for the same analytes in matrix-slurry solutions, even the addition of an extra Rh quantity has resulted in a decrease in the signals. The effect of Triton X-100 (used as a dispersant agent) on analyte intensity and precision was also studied. External calibration from aqueous standards spiked with 100 $\mu\text{g ml}^{-1}$ Rh was performed to quantified 0.010 g/100 ml slurry samples. Results are presented for a certified reference electrical arc furnace flue dust (EAF): CRM-876-1 (Bureau of Analysis Samples Ltd., Cleveland, UK), a reference sample of coke ashes X-3705 (from AG der Dillinger Hüttenwerke, Germany), and a representative sample of EAF flue dust from a Spanish steelmaking company (CENIM-1). For the two reference materials an acceptable agreement with certificate values was achieved, and the results for the CENIM sample matched with those obtained from conventional nebulization solution. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Electrothermal vaporization; Inductively coupled plasma mass spectrometry; Slurry sampling; Steelmaking flue dusts

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1. Introduction

When inductively coupled plasma mass spectrometry (ICP-MS) is used in combination with conventional nebulization of solutions, the complete potential of the technique cannot be fully exploited. To extend its capabilities the application of alternative sample introduction systems was necessary. The use of an electrothermal vaporizer (ETV) as an alternative sampling device possesses several benefits over conventional nebulization (e.g. small sample-size requirements, capability for solid and slurry analysis, ashing-matrix separation, etc.). Indeed, to some extent the advent of micro-nebulizers has displaced ETV as the preferred means of introducing micro-samples into plasmas, however, the ETV sampling technique possesses other unique features which confer capabilities that are not likely to be supplanted in the near future. Nevertheless it also presents crucial aspects; among these limitations, transport loss is one of the most important phenomena which occurs in ETV-ICP-MS. Analyte transport loss has been defined as the fraction of analyte vaporized within the ETV sampling system that does not reach the ICP. Complete vaporization of sample and efficient transport of volatilized material to the ICP are the two most important conditions required to apply ETV as a sampling system for ICP-MS. Kantor [1] described the relationships of the condensation mechanism of vaporized elements to the observed transport loss. The ideal behavior for analyte vaporized from ETV is the rapid self-nucleation to particles being large enough to be effectively transported by the carrier gas and at the same time small enough to avoid deposition in the transport path. Ediger and Beres [2] studied the role of chemical modifiers in analyte transport loss with ETV-ICP-MS. They found that the addition of a modifier was likely to minimize the transport loss of the transfer path. They also present an overview of the trajectory of electrothermal vaporization for ICP from its beginning, with reference to the most important publications which appeared between 1974 and 1992. Sparks et al. [3] considered material lost in the transport tube as a function of the mass of mate-

rial vaporized, with proportionately less loss occurring with larger amounts of vaporized material. In another study, Sparks et al. [4] used an optical laser particle counter in an attempt to verify the loss of material in the transport path; nevertheless, when a carrier was used they found more analyte particles in the transport tube (viz. Ag) than without a carrier. This suggests that without the use of a carrier, part of the analyte remains trapped in some part of the sampling device other than the transport tubing. It must be noted that the real mechanism by which the ETV aerosol is carried to the ICP is not well enough understood.

One of the most notable benefits of ETV as sample device is its capability to perform direct solids analysis. Slurry sample introduction has proven useful as a means of direct solid analysis, since slurries can be prepared directly from finely powdered solids. A multi-element analysis can only be carried out with continuous nebulization if the sample is completely decomposed, this being a very big problem for some materials, as in the case of steelmaking flue dusts. The wide variability of their composition makes a complete and general dissolution procedure rather lengthy and difficult. The usual procedure for dissolving these products, containing carbides and refractory oxides, consists of digesting the sample in an acid mixture and melting the eventual insoluble residue with alkaline fluxes [5], thus producing complex sample matrices with a high content of total dissolved solids. In a previous work [6], the authors evaluated a microwave-assisted heating system to dissolve these types of samples; it was not possible, however, to achieve with any heating program a complete dissolution procedure for the different types of electrical arc furnaces flue dusts (EAFD). Compared with traditional sample dissolution procedures, slurry sampling reduces sample preparation time and the possibility of sample contamination, as well as the risk of analyte loss prior to analysis. Furthermore, slurry sampling combines the benefits of solid and liquid sampling, simplifying sample pretreatment and enabling the use of aqueous calibration solutions.

There is widespread agreement on the criticality of particle size in slurry nebulization studies.

The conclusion of the most rigorous studies is that in slurry nebulization, particles larger than 5 μm do not reach the plasma and this is responsible for the loss of signal. Concerning ICP-MS direct slurry nebulization, partial blockage of the sampling cone is normally found to occur, due to the deposition of particles after a few minutes of nebulization. This results in a decrease in count rate over time. The problem with ETV slurry sampling is quite different to slurry nebulization: particle size seems not to be so extremely critical and cone blockage does not occur. Yongchao et al. [7], in a study related to botanical samples by ETV-ICP-MS, proved that for slurry particles smaller than 170 μm , intensities were identical to those obtained with aqueous solutions.

Gregoire et al. [8] described the direct analysis of solids by slurry electrothermal vaporization ICP-MS highlighting the strengths and weaknesses of this approach, finding the results for most reference materials to be too high when aqueous standards were employed for calibration. Fonseca and Miller-Ihli [9] studied the analyte transport of aqueous solutions and slurry samples, showing that with the use of Pd as a carrier and oxygen ashing for removal of the organic matrix, accurate results were obtainable by using calibration against simple aqueous standards. Hauptkorn et al. [10] developed a method for the determination of relevant trace impurities in high-purity quartz using slurry sampling with a tungsten coil ETV device, concluding that the strong matrix interference represents the main limitation of the technique, needing further improvement through the enhancement of transport efficiency. Chen and Jiang [11] used ultrasonic slurry sampling ETV-ICP-MS to determine Ge, As, Se and Hg in fish samples and investigated the effect of palladium as a modifier on the signals, showing that the signal of Hg increased with the increase in Pd concentration. In contrast, the signals of the other elements decreased slightly with increase in Pd concentrations. In another publication, the same authors [12] determined Hg and Pb in soil samples with the same technique using isotope dilution (ID) determination to overcome the differing sensitivities of soil slurry and aqueous solutions used for

calibration. Pozebon et al. [13] used iridium-coated tubes for the determination of Sn, Sb, Pb and Bi in biological materials, whereas for the other analytes (As, Se, Te, V, Cd, etc.), Pd was used as a carrier/modifier. They found that for most of the sample solutions, 10 μl of a 0.01% m/v Pd solution was efficient for the above elements. Mierza and Yang [14] determined metal impurities in aluminium oxide and compared different calibration procedures, achieving the best results by using the standard addition method. They also tested different modifiers: Pd, Mg, Au and Pt and they did not find any significant effects on the analyte signals. Liaw and Jiang [15] found that Triton not only helped to disperse the slurry particles, but also acted as a physical carrier in sediment slurry samples. Clearly the concentration of the dispersant must be controlled, as an excess can be detrimental to the slurry stability and may be the cause of coagulation [16].

In this study, slurry sampling ETV-ICP-MS was used to determine the concentration of As, Sn, Sb, Bi, Se, Te, Cd, V, Ti and Mo in steelmaking flue dusts. Optimization of the ETV and ICP-MS conditions was performed. A Rh solution was used as a physical carrier and the effect of different concentrations of carrier on analyte transport was evaluated for aqueous solutions and for slurry samples. The effect of Triton X-100 used as dispersant agent, was also studied. The method was applied to the analysis of two reference materials: CRM-876-1 (Bureau of Analysis Samples, UK) and X-3705 (AG der Dillinger Hüttenwerke, Germany). A representative steel-making electrical arc furnace flue dust sample: CENIM-1 was comparatively analyzed with ETV slurry sampling and with a conventional nebulization solution.

2. Experimental

2.1. Instrumentation

A commercial Varian graphite furnace designed for atomic absorption spectrometry (GFAAS: GTA-96, Varian Techtron, Australia Pty Ltd) was coupled to a Perkin Elmer Sciex

Table 1
Experimental conditions for electrothermal vaporization^a

Step	Temperature (°C)	Time (s)
1	75	5
2	90	5
3	150	5
4	150	50
5	275	7.5
6	2900	1.5
7	2900	2
8	40	12.5
9	40	20

^aCarrier Ar flow: 1.8 l min⁻¹ (during all the steps of the ETV cycle).

(Thornhill, Ontario, Canada) ELAN 6000 ICP-MS instrument. Unmodified commercial Varian pyrolytic graphite coated graphite tubes (without plat-forms) were used. Fig. 1 shows a diagram of the transfer line coupling the ETV to the ICP-MS, consisting of a 40-cm length and 4-mm internal diameter Tygon tubing, with a valve system inserted. This valve system allows a practically constant argon flow to the ICP during the different steps of the analysis. During the pre-atomiza-tion steps of the ETV heating program, ETV argon flow was conducted to the waste (flushing volatile sample components from the tube) while an auxiliary Ar flow was send to the plasma. At an established time prior to the vaporization step, the valve system sent the signal to start the ICP-

MS measurement, and the ETV Ar flow was automatically switched to flow to the ICP. The carrier argon outlet adapter was a shaped ceramic probe that provided a smooth transition from the diameter of the ETV cell to the transport tube loading to the ICP. The experimental conditions for ETV and ICP-MS are listed in Tables 1 and 2.

Slurries were shaken with a wrist-action shaker (Baird & Tatlock, Cladwell Heath, Essex, UK) and aliquots were injected with a micro-pipette (Socorex ISBA S.A.).

2.2. Reagents

Nitric acid 70% m/m, doubled distilled, PPB/Teflon grade and Triton X-100 were obtained from Aldrich Fisher (SIGMA-AL-DRICH Quimica S.A., Alcobendas, Madrid, Spain). Multi-element standard calibration solu-tions were prepared from 1 l of commercial 1000 µg ml⁻¹ single-element spectroscopic standard solutions (P. E. Pure Calibration Standards, The Perkin Elmer Corporation, Norwalk, CT). The standard reference materials were: EAF flue dust CRM-876-1 (distributed by the Bureau of Analy-sis Samples Ltd, Cleveland, UK) and coke ashes X-3705 (from AG der Dillinger Hüttenwerke, Dillingen, Germany). EAF flue dust CENIM-1 was provided by Spanish steelmaking.

Table 2
Experimental conditions for ELAN-6000

RF power (W)	1150
Plasma Ar flow (l min ⁻¹)	15
Carrier gas flow (l min ⁻¹)	1.8
Analog stage voltage	– 2000
Pulse stage voltage	1350
Mass spectrometer running pressure (Pa)	3.68 × 10 ⁻⁵
Dwell time per analyte (ms)	10
Sweeps/reading	1
Lens voltage (V)	3.7
Autolens	On
Readings/replicate	75
Analytes:	⁷⁵ As ⁺ , ¹²⁰ Sn ⁺ , ¹²¹ Sb ⁺ , ²⁰⁹ Bi ⁺ , ⁸² Se ⁺ , ¹³⁰ Te ⁺ , ¹¹⁴ Cd ⁺ , ⁵¹ V ⁺ , ⁴⁸ Ti ⁺ , ⁹⁸ Mo ⁺
Estimated reading time (s)	0.22
Estimated replicate time (s)	16.5
Scanning mode	Peak hopping
Signal measurement mode	Peak height

Fig. 1. Diagram of the transfer line coupling the ETV to the ICP-MS. St1: Sample to drain, Ar to plasma; St2: sample to plasma, Ar to drain.

2.3. Preparation of slurries

Portions of 0.010 g of the finely powdered material ($< 20 \mu\text{m}$) were added to 100 ml of a solution containing 0.5% v/v nitric acid and 0.05% v/v Triton X-100. Suspensions were pre-treated by sonication for 15 min using an ultrasonic cell disrupter in order to disintegrate possible particle agglomerates and to complete the dispersion. After and during all the time prior to sampling, slurries were shaken with a wrist-action shaker.

2.4. Multielement standard calibration solutions

Multielement standard calibration solutions of As, Sn, Sb, Bi, Se, Te, Cd, V, Ti and Mo, over a mass range of $0.5\text{--}50 \text{ ng ml}^{-1}$ were prepared. All standards and blanks were prepared fresh daily in a 0.5% v/v nitric acid solution, containing $100 \mu\text{g ml}^{-1}$ of Rh (added as a modifier/carrier) and 0.05% v/v of Triton X-100 (added as dispersant). These solutions were mixed for 10 min with a wrist-action shaker to ensure Triton X-100 homogenization.

3. Results and discussion

3.1. Selection of furnace and plasma conditions

In ETV-ICP-MS, the electrothermal vaporization device serves to thermally pre-treat and vaporize the sample into an argon stream. The vaporized sample flows into the ICP where the complete atomization and ionization processes take place. In this study a commercial atomic absorption graphite furnace was used as a slurry-sampling cell for ICP-MS. Complete vaporization of the sample and efficient transport of volatilized material to the Ar plasma are the most important prerequisites. The design of the system which transports the analytes to the plasma is recognized as one of the main factors influencing effective transport.

The effect of the operating parameters was evaluated by monitoring the transient signals from $10\text{-}\mu\text{l}$ aliquots of a solution containing the analytes As, Cd, Ti and Sn in 50-pg amounts. With regard to the transport path, it was found that decreasing the transport tube length and increasing its internal diameter resulted in an increased sensitivity. The transport path was therefore

shortened to the minimum possible (40 cm) and the internal diameter of the Tygon tubing was established at 4 mm. Since multielement vaporization was performed, sensitivity tests of different vaporization temperatures were carried out in order to select a single and optimum value for all the studied analytes.

Fig. 2 shows the transient signals obtained: (a) using three vaporization temperatures within the same vaporization process (1800, 2600 and 2900°C); and (b) from a single vaporization temperature (2900°C). When different vaporization temperatures were used, within the same vaporization cycle, most of the analytes presented signals in each one of these temperatures. It must be noted that even for ETV-ICP-MS volatile element (e.g. Cd) intensities were achieved heating up to 2900°C, thus permitting multielement analysis using the highest vaporization temperature (2900°C). Using this high vaporization temperature all the injected mass seemed to be vaporized and the system showed very low memory effect.

The influence of the Ar flow rate on signal intensities was also optimized. Tests were conducted using Ar flow rates from 0.85 to 1.8 l min⁻¹ (range allowed by the ETV system used). Fig. 3 shows the behavior of the intensities for As, Sn, Cd and Bi, for Ar flows of 0.85, 1.4 and 1.8 l min⁻¹ (maintaining the Ar flow during all the steps of the electrothermal program, included the vaporization step), and for 1.8* l min⁻¹ stopping the Ar flow rate during the vaporization step. As can be seen, the best sensitivity was obtained at the highest Ar flow available (1.8 l min⁻¹) when it was maintained during all the ETV cycle; this flow also provided well-shaped transient signals and the best R.S.D. values. The ICP-MS conditions were selected to maximize the ion signal while a 10-ng ml⁻¹ multielement solution including Mg, Rh, Pb, Ba and Ce was continuously introduced with a micro-concentric nebulizer with desolvation membrane (D-MCN). Optimization was carried out with a D-MCD because according to a previous work [17] widely different ion lens voltage was required when using dried aerosol compared to wet aerosol (this based on the different ionization conditions between the two sys-

Fig. 2. As, Sn, Cd and Ti transient signals using (a) three vaporization temperatures: 1800, 2600 and 2900°C; and (b) a single vaporization temperature: 2900°C.

tems). After performing the instrumental optimization, the molybdenum oxide rate for the ETV-ICP-MS system was calculated. This study was carried out to evaluate the possible isobaric interference of molybdenum oxides on Cd isotopes. The molybdenum oxide rate was found to be 0.005%, and no significant influence produced by the presence of Mo on Cd signals was observed within the range of tested concentrations.

It was proved that after 60 consecutive measurements using the same graphite tube no significant variation in the intensity of signals occurred. Therefore, regarding the life-time of the tubes, at least 60 vaporization processes could be carried out under the proposed operating conditions.

Fig. 3. Effect of 0.85, 1.4 and 1.8 l min⁻¹ Ar flow rates (maintained during all steps of the electrothermal cycle, included the vaporization step) and of 1.8* l min⁻¹ (stopping the Ar flow during the vaporization step) on As, Cd, Sn and Bi signals.

3.2. Chemical modifier / physical carrier influence

In addition to ETV operating parameters, only one factor was found to affect transport loss; that is the total amount of material present in the electrothermal cell at the time of vaporization. On the basis that the presence of a few micrograms of an element can produce large effects in the transport efficiency, experiments were performed to evaluate this influence. Chemical modifiers are commonly used in ETV-ICP-MS in order to reduce losses of analyte caused by condensation on different parts of the ETV cell or the transfer line that connects the ETV-MS instrument. Although most effects of the modifiers used in ETV-ICP-MS analysis are believed to be physical, it is likely that chemical effects could also be involved in specific instances. In this study Pd and Rh were evaluated to be used as chemical modifiers/physical carriers. Bulska and Jedral [18] have evaluated Pd and Rh-plating of the graphite fur-

Fig. 4. Effect of Rh on As, Sn, Cd and Bi signal intensities. Ten-microliter aliquots containing 50 pg each of the analytes and increasing amounts of Rh were used.

nace showing that Rh modifier causes better thermal stabilization for As and Se, and according to Yang et al. [19], Rh similar to Pd, Ir and Ru, can be readily reduced to their elemental form at low temperatures, probably forming stable intermetallic solid solutions with the analytes during the heating process.

The analytes in 50-pg amounts (10 µl of an aqueous solution containing 5 ng ml⁻¹ of each of the analytes) were vaporized in the presence of varying amounts of Pd and Rh (from 0 to 2 µg). The obtained results showed that both elements are approximately equally efficient as modifier/carrier. The differences in the obtained signal intensities by using Pd or Rh in similar proportions were always within the R.S.D. values. Further experiments were conducted using Rh as modifier/carrier. Fig. 4 shows the effect of different quantities of Rh on the signal intensities of As, Sn, Bi and Cd. The other considered elements showed a similar tendency. The analyte signal intensities were found to increase when increasing Rh concentration between 0 and 0.5 µg,

remaining nearly constant for Rh quantities between 0.5 and 1 μg and presenting a weak decreasing effect for Rh quantities higher than 1 μg . This quantity seems to be large enough to cause signal suppression due to space-charge effects, therefore a high concentration of carrier does not seem to be recommendable. All the tested analytes showed similar behavior, corresponding to the Cd maximum increasing signal (up to 90%). This behavior is in agreement with the results presented by Hughes et al. [20]. Similar results were presented by Nanose and Kubota [21], who found that the Pb signal increased by adding 2 μg Pd.

On the basis of the above study, 1 μg Rh was selected to be added for further vaporization processes. This quantity providing acceptable R.S.D. values ($< 15\%$), and linear calibration graphs with correlation coefficients ≥ 0.999 .

As the method was applied to slurry analysis, the effect of triton X-100 (used as a dispersant agent for slurry preparation) on aqueous solutions was also studied. Triton concentrations of between 0.01% and 0.1% v/v were tested and no significant influence in the analyte intensities was observed. Nevertheless, better R.S.D. values were achieved when Triton was added. This improvement could be explained by the effect of Triton helping to avoid possible flocculatory effects in the multielement standard solutions prepared by mixing single-element solutions in different acid media.

3.3. Benefits of ETV-slurry sampling

For ICP-MS routine analysis, the continuous nebulization technique involving sample decomposition and nebulization of the resulting solution is still the most widely applied in industrial and scientific laboratories. Nevertheless for some materials, as in the case of steelmaking flue dusts, being of an intractable nature, conventional digestion procedures are often complex and potentially hazardous. The direct introduction of slurries into the plasma would circumvent these difficulties and markedly reduce sample preparation time.

Factors of interest to optimize slurry preparation, including material density, particle size and

the distribution of analyte in the slurry, have been considered. The main advantage of EAFD for slurry sampling is the naturally extremely fine particle size (95% have a particle size of $< 1 \mu\text{m}$). This condition makes these products suitable for direct slurry preparation. If conglomerates exist, samples must be initially ground to $< 20 \mu\text{m}$. The density of these materials is relatively high, varying from 1.1 to 2.4 g/cm^3 [22]. Considering a density of 2 g/cm^3 and a particle size of $20 \mu\text{m}$ (assuming a spherical shape of the particles) a 10- μl aliquot of sample slurry would require a minimum of 0.04 mg ml^{-1} of dust to give 50 particles to ensure a representative sampling of the bulk slurry [4]. The effect of nitric acid concentration was investigated by using nitric acid of concentrations ranging from 0.05% to 2% (v/v). Significant positive effects regarding repeatability and precision were not found. With respect to the ion signals, Cd was the only of the studied analytes showing an explicit enhancement. Cd signal intensity increased by a factor of approximately 1.6 from water to 0.5% (v/v) nitric acid and no evident differences were found when more concentrated nitric acid was used. The influence of nitric acid concentration in the rate of the extraction of some of the matrix components, thus affecting the representative sample mass, was also studied. Steelmaking flue dusts can present very different chemical and mineralogical composition, with Fe, Zn and Si being the most common matrix elements. Clearly the rate of the extraction depends on the sample composition. Nitric acid provided significant extraction of Zn oxide and to a lesser extent of some iron oxides. The Zn and Fe amounts extracted (expressed as % of their contents in the tested samples) ranged from $< 5\%$ of the Zn and 3% of the Fe contents (in 0.05% nitric), to approximately 50% of the Zn and 10% of the Fe contents (in 0.5% nitric). Increasing the nitric acid concentration from 0.5 to 2% (v/v) was not found to have a significant effect on the Zn and Fe amounts extracted. The nitric acid concentration used in further slurry preparation was 0.5% (v/v). With the sample proportion proposed for the preparation of slurries (0.010 g/100 ml) the minimum of particles required for sampling representativeness was

ensured, even assuming the partial extraction of some of the matrix components. To avoid flocculatory effects resulting in rapid sedimentation of the finely powdered material, Triton X-100 was employed as a stabilizing agent (dispersant). Triton concentrations varying from 0.01 to 0.1% v/v were tested and, as in the case of aqueous solutions, no influence was observed in analyte sensitivities. Nevertheless, Triton was found to have a clear effect on analyte signal repeatability providing a better precision. The selected concentration was of 0.05% v/v. After preparation and dispersion of a slurry, magnetic stirring is frequently performed whilst the slurry is being sampled, to ensure continuous homogenous distribution of the solid material and to prevent sedimentation. This system cannot always be used for steelmaking flue dusts, because some of these materials may contain magnetic compounds and the use of magnetic stirring would result in migration and even adhesion of some slurry particles to a magnetic stirring bar. In this work slurries were first pre-treated by sonication for 15 min to disintegrate possible agglomerates, and after and during all the time prior to sampling a wrist-action shaker was used as an alternative and effective method to ensure homogeneity and to improve stability of the slurry sample. The concentration of the slurry is an important factor to consider during preparation. Slurries can be diluted, but only within a limited range as the precision may be degraded with slurries that are highly diluted. This is because of the difficulty to obtain reproducible values when the number of particles in the total volume is too low. To evaluate this point, together with the depressing factor due to space-charge effects produced by high quantities of matrix, slurries were prepared from sample CRM-876 with the following concentrations: 0.0025, 0.005, 0.010, 0.015 and 0.020 g/100 ml. Fig. 5 shows As, Cd, Sn and Ti intensities vs. matrix concentration varying from 0.25 μg to 2.0 μg (corresponding to 10 μl of slurries with sample concentrations between 0.0025% m/v and 0.020% m/v); as can be seen for matrix amounts above 1 μg a depressing effect was observed. R.S.D. values > 15% were obtained for all the tested analytes, with

Fig. 5. Effect of the CRM-876 matrix present in a 10- μl slurry aliquot on As, Cd, Ti and Sn signals. All point data are the mean of five measurements.

matrix concentrations between 0.005 and 0.010 g/100 ml. Matrix concentrations below 0.50 μg in the sample aliquot provided higher R.S.D. values. Knowing that the matrix of the slurry itself can act as a physical carrier, tests were also conducted to evaluate the influence of Rh in the slurry solutions. Fig. 6 shows the influence of the addition of Rh carrier to slurries prepared with different proportions of matrix. The results show that the addition of Rh never increases analyte sensitivity in the slurry samples. Moreover, the addition of an extra Rh amount can increase the total mass to an amount resulting in a decrease in the signal, this resulting when both matrix and Rh were present in a total amount greater than 1 μg in the 10- μl aliquot used for the measurement. These results show that the addition of Rh acting as modifier/carrier is not useful for this type of slurry samples due to the fact that the matrix itself is likely to act as a physical carrier. Examination of the plots suggest that the effects of a matrix such as EAFD may be compared with the effect produced by the same amount of Rh acting as modifier/physical carrier.

Fig. 6. Influence of the amounts of Rh and of the CRM-876 sample, present in a 10-µl slurry aliquot on As, Sn, Cd and Ti signals. All point data are the mean of five measurements.

3.4. Calibration graphs and analytical performance

As proved previously, the addition of a low quantity of Rh is beneficial in enhancing analyte sensitivity with aqueous solutions, minimizing the difference in analyte transport between slurries and aqueous solution and enabling the use of aqueous calibration solutions. It was also found that the addition of Triton helped to minimize

the R.S.D. values improving the stability of the solutions.

A series of a blank and six multielement calibration solutions with element concentrations between 0.5 and 50 ng ml⁻¹ were prepared for simultaneous determination of As, Sb, Sn, Bi, Se, Te, Cd, V, Ti and Mo. The blank and all standards were prepared in 0.5% v/v nitric acid and 0.05% v/v Triton X-100 medium and spiked with

Table 3

Calibration report: $y = Ax + B$

Analyte	A (Slope)	B (Inter- cept)	S.D. _A	S.D. _B	Correlation coefficient
As	45 802	1250	1755	1494	0.99921
Sn	163 124	42 404	2100	39 001	0.99897
Sb	113 837	11 823	1195	5848	0.99960
Se	4980	352	210	623	0.99973
Te	51 611	2100	770	1534	0.99985
Bi	384 167	11 357	7953	24 501	0.99916
Cd	23 423	1239	446	1692	0.99905
V	62 086	18 511	1146	10 841	0.99932
Ti	179 734	40 032	3100	47 859	0.99889
Mo	60 609	4245	614	2853	0.99987

100 g ml⁻¹ Rh. Sample aliquots of 10 µl were deposited in the graphite tube, which was heated within the induction furnace by applying the heating program listed in Table 1.

ICP-MS measurements were performed and linear calibration graphs were obtained for all the analytes. The obtained calibration graph parameters are listed in Table 3. The use of an internal standard (Ir and Cs were tested) was found not to be effective enough to improve the analytical performance.

The lowest limits of quantitative analysis expressed as limits of quantification (LOQ) were estimated as the concentration giving a signal equivalent to 10 times the standard deviation of a procedural blank. Table 4 shows the LOQs referred to a 0.010 g/100 ml slurry test sample and the precision (R.S.D., $n = 5$) at concentration levels of 50 times the LOQs. The analytical accu-

Table 4

Limits of quantification ($\mu\text{g g}^{-1}$) based on 10 times the S.D. of a procedural blank, calculated for a 0.010% m/v slurry sample, and precision (R.S.D., $n = 5$) at concentration levels of 50 times the LOQ

Analyte	LOQ ($\mu\text{g g}^{-1}$) 10 $\times$ S.D.	R.S.D. (%) 50 $\times$ LOQ
As	1.1	10.7
Sn	3.6	7.6
Sb	2.1	3.9
Se	2.8	8.3
Te	2.0	12.0
Bi	1.3	8.7
Cd	2.4	8.5
V	5.6	9.3
Ti	7.0	13.3
Mo	3.3	6.7

racy was evaluated by analyzing two certified reference materials: an electrical arc furnace flue dust (CRM-876, Fe–Zn–Pb matrix), and a coke ash (Dillingen X-3705, Si–Al matrix). Table 5 lists the obtained results and the confidence limits (CL, 95%) for $n = 5$; the obtained concentrations showed acceptable agreement with the certified values. To compare slurry-ETV and conventional continuous nebulization, sample CENIM-1 (representative steelmaking EAF flue dust) was analyzed using both sampling systems. Continuous nebulization was applied to a 0.010% m/v solution, obtained with a microwave-assisted acid dissolution procedure [6]. Table 6 shows that for all the tested analytes the slurry-ETV results matched with those obtained from conventional nebulization.

Table 5

Results (%) obtained for the certified elements in reference materials: CRM-876 and Dillingen X-3705 with slurry-ETV-ICPMS, and confidence limits (95% CL, $n = 5$)

Analyte	Sample	Certified (S.D.) (%)	Found (95% CL, $n = 5$) (% $\pm$ CL)
As	CRM-876	0.0231 (0.0014)	0.0210 $\pm$ 0.0025
Sn	CRM-876	0.0942 (0.0042)	0.103 $\pm$ 0.0062
Cd	CRM-876	0.133 (0.009)	0.145 $\pm$ 0.0187
Cd	X-3705	0.0015 (0.0001)	0.0017 $\pm$ 0.00025
V	X-3705	0.0455 (0.0005)	0.042 $\pm$ 0.0037
Ti	CRM-876	0.0478 (0.0042)	0.051 $\pm$ 0.0050
Ti	X-3705	0.689 (0.008)	0.73 $\pm$ 0.087

Table 6

Comparative results ($\mu\text{g g}^{-1}$) in sample CENIM-1 with slurry-ETV-ICPMS and conventional continuous nebulization, and confidence limits (95% CL, $n = 5$)

Analyte	Cont. neb. ^a ($\mu\text{g g}^{-1} \pm \text{CL}$)	Slurry-ETV ($\mu\text{g g}^{-1} \pm \text{CL}$)
As	79 $\pm$ 3	88 $\pm$ 7
Sn	425 $\pm$ 5	440 $\pm$ 20
Sb	100 $\pm$ 3	92 $\pm$ 5
Bi	45 $\pm$ 2	48 $\pm$ 4
Se	21 $\pm$ 1	13 $\pm$ 1
Te	< 0.5	< 2
Cd	418 $\pm$ 5	397 $\pm$ 18
V	138 $\pm$ 4	150 $\pm$ 15
Ti	373 $\pm$ 10	392 $\pm$ 22
Mo	100 $\pm$ 2	94 $\pm$ 7

^aContinuous nebulization using a 0.010% m/v solution, obtained with a microwave-assisted acid dissolution procedure.

4. Conclusion

ETV as a sampling device for ICP-MS, through its ability to use slurries, offers specific capabilities which provide unique features for directly analyzing steelmaking flue dust samples. The analytical capability for the simultaneous determination of elements with very different atomization temperatures from a single atomization process has been demonstrated. The limits of quantification (LOQ) based on 10 times the standard deviation (S.D.) of a procedural blank, calculated for a 0.010 g/100 ml slurry sample varied from 1.1 $\mu\text{g g}^{-1}$ for As to 7.0 $\mu\text{g g}^{-1}$ for Ti. The precision (R.S.D., $n = 5$) at concentration levels of 50 times the LOQ ranged from 3.9% for Sb to 13.3% for Ti. The results obtained from the analysis of two reference materials correspond to an acceptable degree with the certified values and with the results obtained with conventional continuous nebulization. For all the considered analytes (As, Sn, Sb, Bi, Se, Te, Cd, V, Ti and Mo), a good level of sensitivity (in the pg range) and acceptable precision (< 15% R.S.D.) were obtained.

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