*Original Paper*

# Determination of As, Cd, Pb and Tl in coal by electrothermal vaporization inductively coupled plasma mass spectrometry using slurry sampling and external calibration against aqueous standards

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**Abstract.** A method was developed for the determination of As, Cd, Pb and Tl by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) with slurry sample introduction using certified reference coal samples. The $^{75}$As, $^{111}$Cd, $^{208}$Pb and $^{205}$Tl isotopes were monitored, considering the lower probabilities of these isotopes in suffering interferences. The carrier and modifier effect of Ru added in solution was evaluated, demonstrating that sensitivity for all elements is considerably improved by the addition of 15 µg of Ru to each individual measurement. This confirms its ability to act as a physical carrier particularly for the analytes in aqueous solution. Pyrolysis and vaporization temperatures of 500 and 2500 °C, respectively, were selected after optimization for aqueous solutions and for coal slurries. Similarly, the carrier gas flow rate was optimized as 1.1 L min$^{-1}$. After optimization of the operational parameters, the determination of the four elements in six certified reference coal samples was carried out by external calibration against aqueous standards in 5% v/v $HNO_3$, resulting in good agreement between the certified or given values and the determined ones. For Tl, due to the absence of certified values, a comparison was established considering previously published data

using solid sampling high-resolution continuum source graphite furnace atomic absorption spectrometry. Detection limits (µg g$^{-1}$) of 0.1, 0.004, 0.045 and 0.001 were achieved for As, Cd, Pb and Tl, respectively, and the precision was typically better than 10%.

**Key words:** Electrothermal vaporization inductively coupled plasma mass spectrometry; coal; slurry sampling; ruthenium modifier; aerosol carrier.

Coal is employed worldwide as an energy source in thermoelectric power plants, in industries for vapor generation and heating devices, for the extraction of metals and chemicals and as a fuel for transportation systems, among other uses [1]. The use of coal as an energy source is an environmentally hazardous activity from the mining process and transportation to the final storage of ashes, resulting from the combustion process [1]. One of the most hazardous aspects in the use of coal as an energy source is its combustion. In this process, organic components of the matrix are converted into $CO_2$, $H_2O$, HCl, $SO_x$, $NO_x$, CO and traces of other organic substances [2, 3]. The growing consumption of coal, particularly in thermoelectric power plants, implies in an increase of thermal pollution, release of high amounts of particulate matter, sulfur emissions, acid rain and the emission of trace elements

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[4]. Many trace elements (As, Be, Cd, Hg, Mn, Ni, Pb, Se, F, V and U) emitted by thermoelectric power plants and by the domestic and industrial combustion of coal in the cities have well-known toxic effect in living organisms [5].

Trace elements are present in coal in concentrations that differ as a result of several processes by which they have been occluded during the several carbonification stages. Previous studies have shown that 25 environmentally relevant elements may be found in coal in appreciable concentrations, including As, Cd, Pb and Tl, which are classified as potentially hazardous air pollutants by the U.S. Clean Air Act Amendments [4]. Elevated levels of trace elements in soil, vegetation, and water from the leaching process of soil in the proximity of thermoelectric power plants were attributed to the emission of fly ashes, which could be detected at a distance of up to 8 km from the chimney [3]. In this sense, the development of analytical methodologies able to quantify the presence of such elements in coal samples allows not only information regarding its origin, but also the evaluation of potential risks involved in the use of a specific coal.

Trace element concentration in coal samples is, depending on the element, usually low, requiring sensitive instrumental techniques. The most usual form of introduction of samples in most analytical techniques involves bringing the sample into solution, which usually requires the use of acid digestion. Coal samples are particularly difficult to bring into solution, requiring long and complex procedures, which, besides being tedious and time-consuming, result in increased risk of analyte loss, particularly for volatile elements, and involve the safety risk associated to the manipulation of toxic and corrosive substances [6]. Attempts were made to analyze coal samples after acid digestion [7], extraction of trace elements to a mineral phase [8, 9] and even procedures with alkaline fusion [10, 11] and combustion in an oxygen bomb [12], with variable results.

An interesting alternative to these procedures is the use of slurry sampling. Slurry sampling requires only a small amount of complimentary equipment for the preparation of slurries, combining the advantages of conventional liquid sampling (introduction of microvolumes of sample using automatic devices) with those of direct solid sampling (elimination of the digestion step and the problems associated to it) [13]. A single additional step is necessary for slurry sampling procedures, which consists in the homogenization of the slurry prior to the introduction of the sample aliquot in the instrument. Several procedures were described in the literature in order to facilitate this step of the analytical procedure, such as the introduction of stabilizing agents as glycerol [14–16], and the use of magnetic stirring bars [17] and vortex mixing [18]. A few problems were, however, associated with these procedures, such as the adherence of particulate matter on the capillary tip of the autosampler when using stabilizing agents [13], adherence of particles to the magnetic stirring bar [19] and the difficulties associated to the use of autosamplers with vortex mixing [13], resulting mainly in repeatability problems. More efficient methods involve the use of argon [20, 21] and ultrasound probes [22–24]. A limited number of publications dealt with the analysis of coal slurries by ETV-ICP-MS [23, 25] and graphite furnace atomic absorption spectrometry (GF AAS) [26–28].

In ETV-ICP-MS, chemical modifiers are routinely employed with the same purpose as in GF AAS. However, the significant increase in sensitivity for some elements in ETV-ICP-MS using modifiers is probably due to a more efficient transportation of the analyte from the graphite furnace to the plasma torch. This suggests that modifiers can be used in ETV-ICP-MS as in GF AAS, but for ETV-ICP-MS they should be considered in a more general manner, including a new class of modifiers which improves the volatilization process by providing better separation between analyte and matrix and/or improved transportation of the analyte to the plasma. These compounds are classified as physical carriers, acting as condensation sites that allow fast condensation of atoms into particles, therefore improving the transport phenomena [29].

**Table 1.** ICP-MS operating conditions

| | |
|---|---|
| RF power | 1000 W |
| Sampling/skimmer cones | Pt |
| Scan mode | *Peak Hopping* |
| Resolution | 0.7 u (at 10% peak height) |
| Sweeps per reading | 1 |
| Readings per replicate | 80 |
| Replicates | 3 |
| Dwell time | 30 ms |
| Auto lens | On |
| Gas flow rate: | |
| – Principal | 15 L min$^{-1}$ |
| – Intermediate | 1.2 L min$^{-1}$ |
| – Carrier | 1.1 L min$^{-1}$ |
| Dead time | 35 ns |

**Table 2.** HGA temperature program for determination of As, Cd, Pb and Tl in coal slurries (injected sample volume: 20 µL; modifier/carrier volume: 10 µL)

| Step | Temperature/°C | Ramp/s | Hold/s | Ar flow rate/mL min$^{-1}$ | Gas to ICP | Gas to vent |
|---|---|---|---|---|---|---|
| Cleaning | 2650 | 1 | 10 | 300 | | X |
| Cooling[a] | 20 | 1 | 5 | 300 | | X |
| Drying | 90 | 10 | 10 | 300 | | X |
| Drying | 130 | 10 | 10 | 300 | | X |
| Pyrolysis | 500 | 5 | 25 | 300 | | X |
| Cooling | 20 | 2 | 5 | 300 | | X |
| Vaporization[b] | 2500 | 0.5 | 8 | 300 | X | |
| Cooling | 20 | 2 | 5 | 300 | X | |

[a]Injection step; [b]reading step.

In this work, the analysis of coal samples is described using slurry sampling and ruthenium as modifier/carrier to determine As, Cd, Pb and Tl by ETV-ICP-MS using external calibration against aqueous standards.

## Experimental

### Instrumentation

All measurements were carried out in an inductively coupled plasma mass spectrometer (ICP-MS) Elan 6000 (Perkin Elmer – Sciex, Thornhill, ON, Canada – www.perkinelmer.com), equipped with an HGA 600MS electrothermal vaporization (ETV) device and an AS-60 autosampler, all from Perkin Elmer. The ETV was connected to the ICP-MS by means of a 60-cm long PTFE tube with an internal diameter of 0.5 cm. Pyrolytically coated graphite tubes (Perkin Elmer, B050 8371) were used. Daily performance check was carried out prior to each working day using conventional pneumatic nebulization. Argon 99.996% (White Martins, São Paulo, SP, Brazil – www.whitemartins.com.br) was used exclusively. The ICP-MS operating parameters were set as listed in Table 1. The temperature program for the ETV device is shown in Table 2.

### Reagents and certified reference materials

All reagents used were of analytical grade. Nitric acid (Carlo Erba, Milan, Italy, no. 4080150 – www.carloerbareagenti.com) was doubly distilled by sub-boiling distillation in a quartz still (Kürner Analysentechnik, Rosenheim, Germany). De-ionized water with a resistivity of 18 MΩ cm was produced in a Milli-Q system (Millipore, Bedford, MA, USA – www.millipore.com). Stock standard solutions containing 1000 mg L$^{-1}$ As, Cd, Pb and Tl were prepared by the appropriate dissolution of high-purity $As_2O_3$, CdO, $Pb(NO_3)_2$ and $TlNO_3$, respectively (SPEX, Eddison, NJ, USA – www.spex.com). A 1000 mg L$^{-1}$ ruthenium solution (Fluka, Buchs, Switzerland – www.sigmaaldrich.com) was used as supplied. Calibration solutions were prepared after proper dilution in 5% v/v $HNO_3$.

The following certified reference materials (CRM) were used: SARM 18 "Coal Witbank", SARM 19 "Coal O.F.S." and SARM 20 "Sasolborg Coal" (South Africa Bureau of Standards, Pretoria, South Africa); BCR 182 "Steam Coal" (Community Bureau of Reference, Brussels, Belgium); and NIST 1630a "Trace Mercury in Coal" and NIST 1635 "Trace Elements in

Coal – Subbituminous" (National Institute of Standards and Technology, Gaithersburg, MD, USA).

### Procedure

Coal samples were ground in an agate mortar and passed through a polyester sieve for particle diameter ≤50 µm. Afterwards, aliquots containing approximately 50 mg of each sample were weighed and transferred to 15-mL polypropylene tubes, followed by the addition of 500 µL of concentrated $HNO_3$. De-ionized water was then added up to 5 mL and the mixture was submersed in an ultrasound bath for
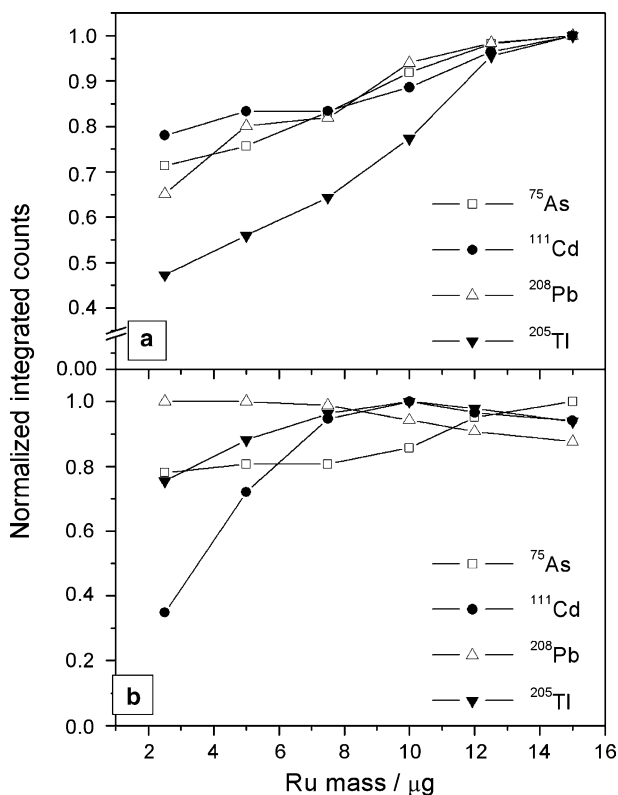


**Fig. 1.** Effect of Ru mass on the normalized signal obtained by ETV-ICP-MS for $^{75}$As, $^{111}$Cd, $^{208}$Pb and $^{205}$Tl in: (a) aqueous solution (20 µg L$^{-1}$) and (b) 5 mg mL$^{-1}$ SARM 20 coal slurry, at a pyrolysis temperature of 500 °C. Normalized counts: ratio between the individual count and the maximum count

30 min. Later, de-ionized water was added to make up the final volume to 10 mL. Slurries were manually agitated and left to stand until use.

Prior to each injection, slurries were homogenized manually using a micropipette and 20 μL were inserted into the graphite tube using the autosampler. For each aliquot of the slurry, 15 μL of the 1000 mg L$^{-1}$ Ru stock solution were injected into the graphite tube. The temperature program in Table 2 was run after each injection.

## Results and discussion

### Optimization of carrier/modifier mass

Aiming to obtain maximum sensitivity and thermal stability for the four analytes, Ru was chosen to act both as a modifier and as a carrier for the procedure. The effect of increasing masses of Ru inserted into the graphite tube on the intensity signals of the four analytes is shown in Fig. 1a. In this figure, it is evident that the highest sensitivity for all analytes in aqueous solution can be achieved using 15 μg Ru, the highest

mass investigated, on each measurement cycle. A similar behavior was observed for As, Cd and Pb with the addition of Ru, although for Cd the absence of the modifier results in a dramatically reduced sensitivity (essentially no signal can be detected for Cd without Ru). The element with a higher dependence on the Ru mass added was Tl, for which the sensitivity with the addition of only 2.5 μg is about 50% of the sensitivity achieved under optimum conditions (i.e., 15 μg Ru). The results demonstrate that within the Ru mass range studied, apparently there is no significant transport loss, mass discrimination effect or plasma loading due to the large excess of added carrier or these effects have been overcompensated by the higher transport efficiency.

This same optimization was carried out for SARM 20 coal slurry, and the results are depicted in Fig. 1b. It is evident, in this case, that the addition of Ru affects the sensitivity for the four analytes, although
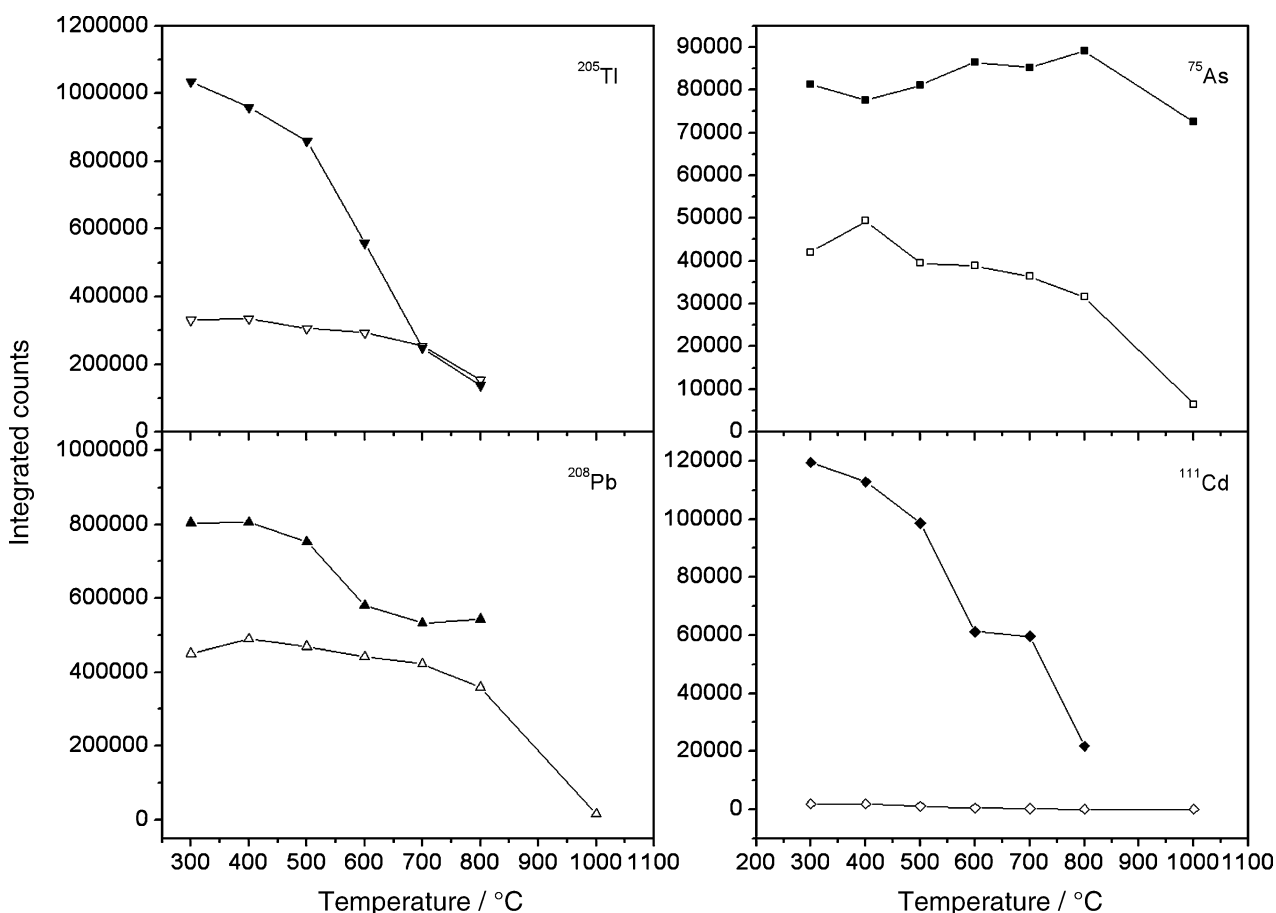


**Fig. 2.** Pyrolysis curves for $^{75}$As, $^{111}$Cd, $^{208}$Pb and $^{205}$Tl in 5% v/v HNO$_3$ aqueous solution (20 μg L$^{-1}$ of each analyte) obtained by ETV-ICP-MS without modifier (open symbols) and with the addition of 15 μg Ru as carrier/modifier (full symbols). Vaporization temperature: 2500 °C

the effect is less pronounced than for aqueous solutions, probably due to the fact that the coal matrix itself acts as a carrier and, therefore, further addition of Ru does not influence the analyte signal on the same magnitude as it does for aqueous solutions. The only exception in the case of SARM 20 coal is Cd, which is the most volatile analyte studied, and the pronounced increase in sensitivity with increasing Ru mass may be attributed to a great extent to thermal stabilization at the pyrolysis stage.

*Pyrolysis temperature*

Pyrolysis curves for As, Cd, Pb and Tl in aqueous solution with and without the addition of Ru are shown in Fig. 2. Despite the fact that thermal stabilization is not significantly high with the use of Ru, the signal increase is evident for the four analytes, demonstrating that Ru may act as an aerosol carrier with high efficiency. This effect is significantly pronounced for Cd, for which a signal 2 orders of magnitude higher is
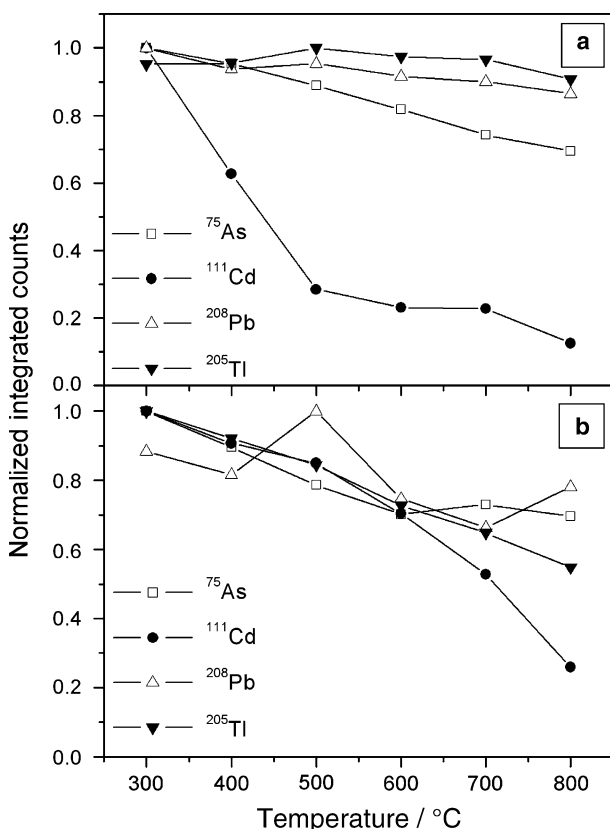


**Fig. 3.** Pyrolysis curves for $^{75}$As, $^{111}$Cd, $^{208}$Pb and $^{205}$Tl in 5 mg mL$^{-1}$ SARM 20 coal slurry in 5% v/v HNO$_3$ obtained by ETV-ICP-MS (a) without modifier and (b) with the addition of 15 µg Ru as carrier/modifier. Vaporization temperature: 2500 °C

achieved using Ru as carrier – essentially no Cd could be detected in the absence of Ru. It is worth to mention that measurements were made for the $^{111}$Cd isotope, which has a natural abundance of only 12.75%, as the two main Cd isotopes suffer from isobaric overlapping interference from $^{112}$Sn and $^{114}$Sn. Nevertheless, the use of Ru as carrier allowed high sensitivity to be obtained, without any apparent prejudice to the precision. The pyrolysis curves in Fig. 2 also show that a higher thermal stability was achieved for As using Ru.

Pyrolysis curves for SARM 20 coal slurry are shown in Fig. 3. The thermal stability for As, Pb and Tl is rather the same without the use of a modifier (Fig. 3a), but for Cd, losses of about 40% can be detected already at 400 °C. With the use of 15 µg of Ru, as shown in Fig. 3b, a pyrolysis temperature of 500 °C can be applied for all analytes without significant losses, and particularly Cd is considerably thermally stabilized. A reduction of around 25–30% in the analytical signal occurs already at a pyrolysis temperature of 600 °C, which restricts the use of more elevated temperatures for these analytes. This decrease in sensitivity with increasing temperatures can be ascribed not only to analyte volatilization, but also to a reduction in the amount of matrix in the graphite tube prior to the vaporization stage. As the coal matrix itself may act as an aerosol carrier, a reduction in the analytical signal could be expected as higher amounts of matrix are eliminated from the graphite tube at the pyrolysis stage, which seems to be particularly the case when Ru is used as the modifier/carrier, as it apparently increases the volatility of the matrix. On the other hand, pyrolysis temperatures below 500 °C may lead to the deposition of carbon in the cones and lens, once the solid material remaining from the pyrolysis stage is carried to the plasma during the vaporization step. As a compromise between these two effects, a pyrolysis temperature of 500 °C was adopted for both calibration solutions and slurries.

*Vaporization temperature*

The vaporization temperature was optimized for the four analytes in aqueous solution and in SARM 20 coal slurry using Ru. The results are shown in Fig. 4. In Fig. 4a, it can be seen that the vaporization temperature has little influence on the analytical signal within the temperature range studied (2000–2600 °C) for aqueous solutions, except for As, which reaches a maximum signal at 2600 °C. A similar behavior is
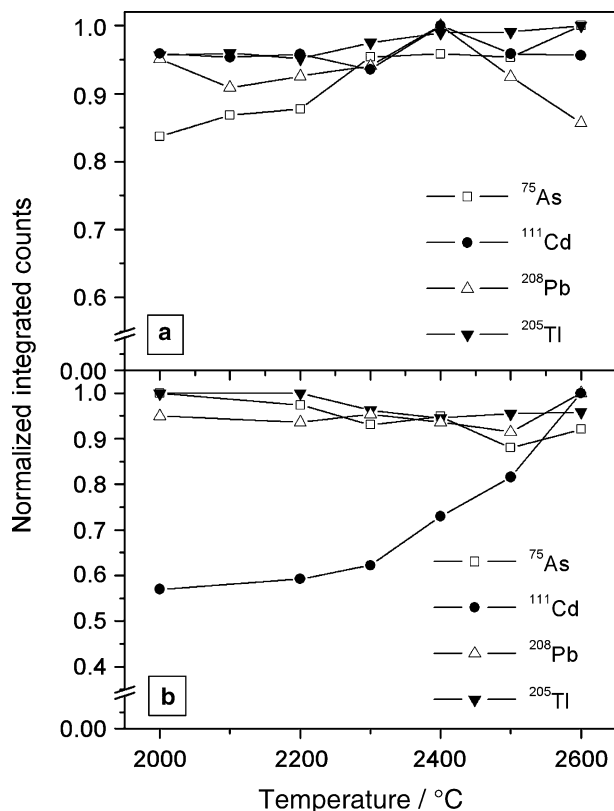
**Fig. 4.** Vaporization curves for [75]As, [111]Cd, [208]Pb and [205]Tl obtained by ETV-ICP-MS in: (a) 5% v/v $HNO_3$ aqueous solution (20 µg L$^{-1}$ of each analyte), and (b) 5 mg mL$^{-1}$ SARM 20 coal slurry. Pyrolysis temperature: 500 °C

observed for SARM 20 coal slurry (Fig. 4b), with little influence of the vaporization temperature on the analytical signal, except for Cd, for which the maximum signal is obtained at 2600 °C. Possibly, the higher dependency of the analytical signal on the vaporization temperature for Cd can be explained by the more efficient vaporization of the carrier at higher temperatures, as this element has shown to be highly dependent on the carrier effect. As a compromise, the vaporization temperature was set to 2500 °C.

### Optimization of the carrier gas flow rate

The effect of the carrier gas flow rate within the range 0.8–1.4 L min$^{-1}$ which does not include the internal Ar flow rate of 300 mL min$^{-1}$, on the analytical signal of the four analytes was evaluated. The results are shown in Fig. 5, which demonstrates that, except for Cd, a flow rate of 1.1 L min$^{-1}$ results in higher signals. For Cd, there is a 10% enhancement in the analytical signal at a carrier gas flow rate of 1.2 L min$^{-1}$. The reduction in the analytical signal observed for flow rates above



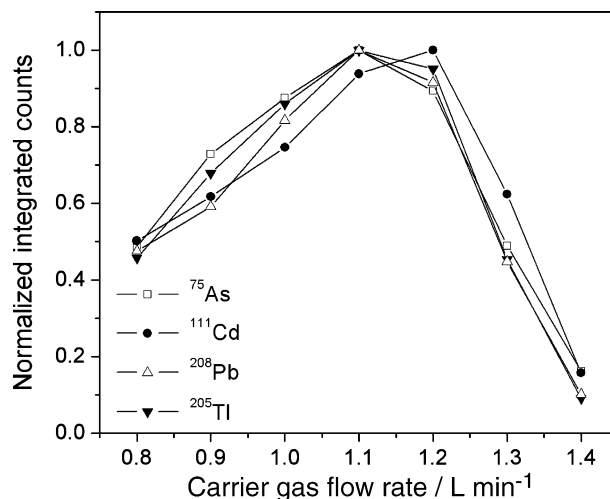**Fig. 5.** Influence of the carrier gas flow rate on the normalized signal obtained by ETV-ICP-MS for [75]As, [111]Cd, [208]Pb and [205]Tl in 5% v/v $HNO_3$ aqueous solution (20 µg L$^{-1}$ of each analyte) with the addition of 15 µg Ru as carrier/modifier.

1.1 L min$^{-1}$ (1.2 L min$^{-1}$ for Cd) is possibly a consequence of the reduction in the residence time of the analyte species in the plasma, resulting in lower ionization degree. The use of elevated nebulizer flow rates also implies in the displacement of the plasma sampling zone to regions of lower temperature, which are more subject to interference. An inverse effect should be expected at lower nebulizer flow rates, but favoring the formation of doubly-charged ions. As a compromise, the nebulizer flow rate was adjusted to 1.1 L min$^{-1}$.

### Results

The results obtained for As, Cd, Pb and Tl in CRM slurries are shown in Table 3. As can be seen, there is good agreement between certified or informed values and the values obtained by slurry sampling ETV-ICP-MS using external calibration against aqueous standards at a statistical confidence level of 95%, except for Cd in BCR 182, which resulted in a value about 40% lower than the certified value. Particularly for Cd in SARM 19, SARM 20 and NIST 1630a, the results were compared to those obtained using direct solid sampling high-resolution continuum source graphite furnace atomic absorption spectrometry (SS-HR-CS GF AAS) [30], as no reference values were available for those samples.

None of the analyzed coal samples had certified or informed concentration values for Tl, and the results were also compared with previously published results obtained using SS-HR-CS GF AAS [31]. In all cases,

**Table 3.** Results ($\mu$g g$^{-1}$; $n = 5$) obtained for As, Cd, Pb and Tl in coal by ETV-ICP-MS with slurry sampling in 5% v/v HNO$_3$ using 15 $\mu$g Ru as modifier/carrier and external calibration against aqueous standards

| Sample | As | | Cd | | Pb | | Tl | |
|---|---|---|---|---|---|---|---|---|
| | Certified | Found | Certified | Found | Certified | Found | Reference value[c] | Found |
| SARM 18 | 0.93[a] | 0.99 ± 0.15 | 0.23[a] | 0.11 ± 0.01 | 5* | 4.87 ± 0.48 | 0.09 ± 0.01 | 0.10 ± 0.01 |
| SARM 19 | 7 (6–8) | 7.8 ± 0.5 | 0.13 ± 0.02[b] | 0.096 ± 0.011 | 20 (17–23) | 21.1 ± 0.5 | 0.62 ± 0.01 | 0.63 ± 0.01 |
| SARM 20 | 4.7 (4.6–6.0) | 4.7 ± 0.5 | 0.05 ± 0.01[b] | 0.03 ± 0.01 | 26 (20–29) | 26.1 ± 1.8 | 0.34 ± 0.01 | 0.43 ± 0.04 |
| BCR 182 | 1.47* | 1.83 ± 0.17 | 0.057 ± 0.004 | 0.034 ± 0.004 | 15.3* | 15.9 ± 0.7 | 0.09 ± 0.01 | 0.13 ± 0.04 |
| NIST 1630a | – | 13.5 ± 1.2 | 0.073 ± 0.003[b] | 0.071 ± 0.01 | – | 4.9 ± 0.5 | 0.46 ± 0.02 | 0.41 ± 0.05 |
| NIST 1635 | 0.42 ± 0.15 | 0.56 ± 0.09 | 0.03 ± 0.01 | 0.05 ± 0.01 | 1.9 ± 0.2 | 2.0 ± 0.4 | 0.01 ± 0.01 | 0.012 ± 0.001 |

*Informed value; [a]from Ref. [32]; [b]from Ref. [30]; [c]from Ref. [31].

there is a good agreement between the adopted reference values and the values obtained by ETV-ICP-MS, which is yet another indication that external calibration against aqueous standards, which is simpler, faster and less expensive than other calibration techniques such as isotope dilution, can be successfully applied to this procedure.

### Analytical figures of merit

The analytical figures of merit are shown in Table 4, calculated from the regression equations for the calibration curves against aqueous standards. As can be seen, the highest sensitivity was obtained for Pb and Tl. Detection limits (LOD) in the order of ng g$^{-1}$, calculated for the samples, demonstrate the high sensitivity of the proposed procedure, allowing its application to determine the four analytes at trace levels in coal samples. For Cd, although an inferior sensitivity has been obtained as a consequence of measurements using an isotope of lower abundance, the good precision resulted in very low LOD. The lowest LOD was achieved for Tl, demonstrating the excellent sensitivity for this element. Thallium may be particularly affected by the use of commonly employed halogen-containing carriers such as NaCl, as the salts of this element are volatile at low temperatures. For As, the higher LOD may be a consequence of the higher ionization energy, resulting in lower sensitivity and a consequently higher LOD. Nevertheless, the method resulted in LOD values from 5 to 27 times better in comparison

to those shown in a previous publication by Maia et al. [23] for Cd, Pb and Tl using isotope dilution, and comparable LOD values for As and Pb to those obtained using external calibration [25]. The precision was typically better than 15%.

### Conclusions

Slurry sampling has proved to be a simple and fast procedure to determine As, Cd, Pb and Tl in coal samples by ETV-ICP-MS. Ruthenium can act as a physical carrier when added to each injection cycle, allowing higher transport efficiency of the four analytes particularly for aqueous solutions. Under these conditions, the determination can be carried out successfully using external calibration against aqueous standards, as attested by a good agreement between reference and found values for the analytes in six CRM. Good detection limits were obtained for all analytes, demonstrating that despite the dilution which is applied, the method is extremely sensitive and applicable to coal samples. It should be expected that this same procedure could be extended to the determination of other analytes in coal samples using ETV-ICP-MS.

**Table 4.** Figures of merit for the proposed procedure

| | $^{75}$As | $^{111}$Cd | $^{208}$Pb | $^{205}$Tl |
|---|---|---|---|---|
| Slope (L $\mu$g$^{-1}$) | $1.4 \times 10^4$ | $9.4 \times 10^3$ | $1.2 \times 10^5$ | $1.7 \times 10^5$ |
| R | 0.9998 | 0.9992 | 0.9999 | 0.9998 |
| LOD ($\mu$g g$^{-1}$) | 0.1 | 0.004 | 0.045 | 0.001 |

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