

Accepted Manuscript

Determination of Se at low concentration in coal by collision/reaction cell technology inductively coupled plasma mass spectrometry

Alessandra S. Henn, Filipe S. Rondan, Marcia F. Mesko, Paola A. Mello, Magali Perez, Joseph Armstrong, Liam A. Bullock, John Parnell, Joerg Feldmann, Erico M.M. Flores

PII: S0584-8547(17)30501-3
DOI: doi:[10.1016/j.sab.2018.02.014](https://doi.org/10.1016/j.sab.2018.02.014)
Reference: SAB 5383

To appear in: *Spectrochimica Acta Part B: Atomic Spectroscopy*

Received date: 27 October 2017
Revised date: 21 February 2018
Accepted date: 23 February 2018

Please cite this article as: Alessandra S. Henn, Filipe S. Rondan, Marcia F. Mesko, Paola A. Mello, Magali Perez, Joseph Armstrong, Liam A. Bullock, John Parnell, Joerg Feldmann, Erico M.M. Flores , Determination of Se at low concentration in coal by collision/reaction cell technology inductively coupled plasma mass spectrometry. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Sab(2017), doi:[10.1016/j.sab.2018.02.014](https://doi.org/10.1016/j.sab.2018.02.014)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



**Determination of Se at Low Concentration in Coal by
Collision/reaction Cell Technology Inductively Coupled Plasma
Mass Spectrometry**

*Alessandra S. Henn^a, Filipe S. Rondan^b, Marcia F. Mesko^b, Paola A. Mello^a, Magali Perez^c,
Joseph Armstrong^d, Liam A. Bullock^d, John Parnell^d, Joerg Feldmann^c, Erico M. M. Flores^{a*}*

^a Departamento de Química, Universidade Federal de Santa Maria, 97105-900, Santa Maria, RS, Brazil

^b Centro de Ciências Químicas, Farmacêuticas e de Alimentos, Universidade Federal de Pelotas, 96010-610, Pelotas, RS, Brazil

^c Trace Element Speciation Laboratory (TESLA), Department of Chemistry, University of Aberdeen, King's College, Aberdeen, AB24 3UE, Scotland, UK

^d Department of Geology & Petroleum Geology, Meston Building, University of Aberdeen, King's College, Aberdeen, AB24 3UE, Scotland, UK

*Corresponding author: Tel: +555532209445

Email address (Erico M. M. Flores): ericommf@gmail.com

Abstract

A method is proposed for the determination of selenium at low concentration in coal by collision/reaction cell technology inductively coupled plasma mass spectrometry (CRC-ICP-MS). Samples were decomposed by high pressure microwave-assisted wet digestion (MAWD) using 250 mg of coal, a mixture of 5 mL of 14.4 mol L⁻¹ HNO₃ and 1 mL of 40% HF and 70 min of heating program (200 °C and 40 bar). Hydrogen gas used in the collision/reaction cell was investigated to minimize the argon-based interferences at m/z 77, 78 and 80. The rejection parameter (RPq) and the H₂ gas flow rate were set to 0.45 and 4.8 mL min⁻¹, respectively. The use of H₂ in the cell resulted in other polyatomic interferences, such as ⁷⁶Ge¹H⁺, ⁷⁹Br¹H⁺ and ⁸¹Br¹H⁺, which impaired Se determination using ⁷⁷Se, ⁸⁰Se and ⁸²Se isotopes, thus Se determination was carried out by monitoring only ⁷⁸Se isotope. Selenium determination was performed in certified reference materials of coal (NIST 1635 and SARM 20) and an agreement better than 95% was observed between the results obtained by CRC-ICP-MS and the certified values. Under optimized conditions, the instrumental limit of detection was 0.01 µg L⁻¹ and the method limit of detection was 0.01 µg g⁻¹, which was suitable for Se determination at very low concentration in coal.

Keywords: Coal; Selenium determination; CRC-ICP-MS; Collision/reaction cell; Selenium interferences.

1. Introduction

Coal has been used worldwide as an energy source in thermoelectric power plants, in industries for vapor generation, as a fuel for some transportation systems, among other uses. Elements, such as selenium can be present in coal. These elements can be released to the atmosphere during coal combustion or can be concentrated in the inorganic fraction [1, 2]. Selenium is a naturally occurring element that is an essential trace element of fundamental importance to human biology but can be toxic at high concentrations [3]. On the other hand, Se can be recovered from coal and coal combustion products to be used in industrial applications [4, 5]. However, the development of analytical methods to provide the determination of this element in low concentration is still a challenging task, due to the difficulty to digest coal, as well as the drawbacks involved in Se determination.

Most of the studies have reported the determination of Se in coal by atomic spectrometric techniques, such as atomic fluorescence spectrometry (AFS), hydride generation atomic absorption spectrometry (HG AAS) [6], and inductively coupled plasma optical emission spectrometry (ICP-OES) [7, 8]. However, these techniques present some disadvantages, such as relatively poor limits of detection (LODs) and low throughput.

Inductively coupled plasma mass spectrometry (ICP-MS) is frequently used for multi-element determination in coal, providing low LODs and a wide linear range [7-9]. However, ICP-MS has also some limitations such as the occurrence of spectral and non-spectral interferences [10]. The plasma gas (Ar), matrix components and solvent ions, can generate polyatomic interferences [10, 11]. Selenium presents six isotopes (^{74}Se , ^{76}Se , ^{77}Se , ^{78}Se , ^{80}Se and ^{82}Se) and all of them have potential interferences. As can be seen in Table 1, major interferences are argon-based molecular ions [10, 12]. In order to overcome these interferences, some approaches such as the use of (i) mathematical corrections, (ii) cold

plasma conditions, and (iii) collision/reaction interface have been proposed [13, 14]. Alternatively, technologies such as high resolution sector field ICP-MS (HR-SF-ICP-MS) and triple quadrupole ICP-MS (ICP-MS/MS) can also be applied for interferences correction. However, these instruments have higher cost than quadrupole-based instruments, and are therefore more difficult to be implemented in routine laboratories [15-18].

Table 1

Collision/reaction cell technology (CRC) has been widely used to minimize the argon-based interferences in ICP-MS determination [19, 20]. In this case, a collision/reaction gas (helium, hydrogen, ammonia, oxygen, methane) is injected into the cell, which collides and reacts with polyatomic ions. By different ion-molecule collisions followed by kinetic energy discrimination (KED) and ion-molecule chemistry, polyatomic ions are converted into non-interfering species that are ejected from the cell. In addition, the analyte can also be converted into another ion that is not prone to interference [19]. This technology has been successfully applied to the determination of Se in various matrices [21-25]. However, there is a lack of works showing the application of CRC for Se determination in a difficult matrix as coal. This is particularly challenging when considering the difficulties for the digestion of coal. Microwave-assisted wet digestion (MAWD) is the most frequently used method for coal digestion [7, 8, 21, 26-28]. Coal digestion usually requires a high amount of concentrated acids, as HNO₃, HF and HCl and high temperature and pressure. However, the final digests can present a high residual acidity and carbon content, which can cause interferences [29]. High carbon content can cause signal enhancing effects due to charge transfer reactions involving carbon-containing charged species in the plasma [30, 31]. Moreover, hydrofluoric acid can damage the nebulizer and quartz torch of the spectrometric techniques, requiring a

dilution step, which impairs the method limit of detection. In addition, the sample mass that can be digested is usually in the range of 200 to 300 mg [32-34].

In this sense, the aim of this work was to demonstrate the feasibility of CRC-ICP-MS with hydrogen as a collision/reaction gas for Se determination at low levels in coal after decomposition by MAWD. The hydrogen flow rate and the parameters of the cell were evaluated in order to find the best conditions. The accuracy was evaluated by using certified reference material (CRM) of coal and by comparison with results obtained by ICP-MS monitoring the most abundant Se isotope with less interference at m/z 82.

ACCEPTED MANUSCRIPT

2. Experimental

2.1. Instrumentation

The determination of Se was performed using a quadrupole-based inductively coupled plasma mass spectrometer (NexION 300X[®], Perkin Elmer, Canada) equipped with a concentric nebulizer (Meinhard, USA), a cyclonic spray chamber (Glass Expansion, Inc., Australia) and a quartz torch with a quartz injector tube (2 mm i.d.). This instrument was also equipped with a cell that can be used both as a collision/reaction cell technology and as a dynamic reaction cell (DRC). Argon (99.998%, White Martins, Brazil) was used for plasma generation, nebulization and as auxiliary gas. The instrumental parameters selected for analysis by ICP-MS and by CRC-ICP-MS are shown in Table 2.

Table 2

Additionally, an inductively coupled plasma optical emission spectrometer (model Spectro Ciros CCD, Spectro Analytical Instruments, Germany) was used for the measurement of carbon content in digests. The instrument was equipped with a cross-flow nebulizer coupled to a Scott double-pass type spray chamber. Radiofrequency (RF) power and plasma, auxiliary and nebulizer gas flow rate were set at 1300 W, 12.0, 1.0 and 1.0 L min⁻¹. Carbon content in digests was determined by using the wavelength 193.030 nm and Y at 371.029 nm was used as internal standard [35, 36].

Coal was digested by MAWD using a microwave oven (Multiwave3000[®], Microwave Sample Preparation System, Anton Paar, Austria, software version v1.27-Synt) equipped with up to sixteen PTFE vessels with 100 mL of internal volume and maximum operational temperature and pressure of 220 °C and 40 bar, respectively. An analytical balance (AY 220, Shimadzu, Japan, 220 g, 0.0001 g of resolution) was used for weighing samples.

Total acid concentration in digests was determined by titration using an automatic titrator (Titrand 836, Metrohm, Switzerland) equipped with a module for automatic stirring (803 Ti Stand, Metrohm), a dosing device of 20 mL (Dosino 800, Metrohm) and a combined pH electrode (6.0262.100, Metrohm).

2.2. Reagents and samples

Water was purified using a Milli-Q system, (Millipore, USA, 18.2 M Ω cm) and it was used to prepare all standard solutions and reagents. Concentrated HNO₃ (65%, 1.4 kg L⁻¹, Merck, Germany) was distilled in a sub-boiling system (DuoPur, Milestone, Italy), which was used for MAWD and for the preparation of reference solutions. Hydrofluoric acid (40%, 1.15 kg L⁻¹, Sigma Aldrich, USA) was used without previous purification for digestion by MAWD. Calibration was performed by external calibration using reference solutions of Se (0.01 to 10 μ g L⁻¹) which were prepared by sequential dilution of a stock solution (1000 mg L⁻¹, Merck) in 5% HNO₃. Potassium hydroxide (Merck) was used to prepare a 0.1 mol L⁻¹ solution for residual acidity determination. For carbon determination, a stock reference solution of 1000 mg L⁻¹ was prepared by dilution of citric acid (Merck) in water. Calibration was performed with a standard solutions prepared by sequential dilution (5 to 500 mg L⁻¹) of a stock reference solution, and 1 mg L⁻¹ of yttrium was used as internal standard. Hydrogen (99.999%, White Martins, Brazil) was used in the collision/reaction cell.

Coal samples were obtained from coal deposits from the United Kingdom and were named from "A" to "J". Samples were ground using a cryogenic mill (model 6750, Spex Certiprep, USA), with 2 min of pre-cooling time followed by 3 min for grinding. This last procedure was repeated three times. Samples were dried at 105 °C for 2 h in an oven (model 400/2ND, Nova Ética, Brazil) before use. The accuracy was evaluated using two certified reference materials: NIST 1635 (subbituminous coal) from National Institute of Standards and

Technology and SARM 20 (coal) from Council for Mineral Technology, Republic of South Africa.

2.3. Sample preparation

Coal samples and CRMs used for the optimization and accuracy evaluation of the CRC-ICP-MS method were digested by microwave-assisted wet digestion (MAWD). In this way, 250 mg of coal were weighed inside PTFE vessels and 5 mL of 14 mol L⁻¹ HNO₃ and 1 mL of 40% HF were added. The heating program was performed as follows: step *i*) 1400 W for 40 min (ramp of 10 min); and step *ii*) 0 W for 20 min (cooling step). The exhaustion of microwave oven was kept at 60 m³ air h⁻¹ during the heating program and at 125 m³ air h⁻¹ in the cooling step. After digestion, dilution with water up to 25 mL was carried out for Se determination by ICP-MS and CRC-ICP-MS.

2.4. CRC-ICP-MS optimization

Initial optimization was based on the signal intensities for Se isotopes and for the background, using H₂ into the collision cell. The effect of H₂ gas flow rate introduced into the CRC on the signal to noise (S/N) ratio of Se isotopes was evaluated. This study was performed using a reagent blank prepared with 5% HNO₃ and a digested coal sample (Coal A) obtained by MAWD (250 mg of coal, 25 mL final volume, 10 times diluted). The results for digested sample (Coal A) were normalized by the concentration of Se in the sample. The H₂ gas flow rate was evaluated from 0.2 to 5.0 mL min⁻¹. Hydrogen gas flow rates higher than 5 mL min⁻¹ were not evaluated, because they caused a variation in the vacuum pressure of the ICP-MS instrument. Data for each condition were acquired in triplicate, monitoring Se isotopes, at $m/z = 77, 78, 80$ and 82 . The rejection parameter RP_q of the cell was evaluated

from 0.05 to 0.9. After optimization, conditions described in Table 2, were selected and the digested samples and CRMs were analyzed.

3. Results and Discussion

3.1. Determination of Se in coal using standard mode ICP-MS

Coal samples and CRMs (NIST 1635 and SARM 20) used in this work were decomposed by MAWD to obtain suitable digests for the optimization of the CRC-ICP-MS method. When operating ICP-MS at the conventional mode, the determination of Se was carried out by monitoring Se at m/z 77 or 82. This was due to the presence of a large argon-based background at m/z 78 and 80, due to $^{40}\text{Ar}^{38}\text{Ar}^+$ and $^{40}\text{Ar}_2^+$, respectively. Furthermore, an interference caused by chlorine at m/z 77 can also be observed due to the formation of $^{40}\text{Ar}^{37}\text{Cl}^+$ [10]. In this way, Se determination by standard mode ICP-MS was performed by using ^{82}Se and the results are shown in Table 3. In addition, Table 3 also shows the concentration of possible interferences and elements that are usually present at high concentration in coal, such as Br, Fe and Pb. Bromine content in coal samples was determined by ICP-MS after digestion by microwave-induced combustion, following previous works [37, 38]. The concentration of Fe was determined by ICP-OES and Pb by ICP-MS in digests obtained after MAWD.

Table 3

Results obtained for coal samples showed that Se content in analyzed coals was relatively low ranging from < 1.5 to $5.87 \mu\text{g g}^{-1}$. Selenium can occur in coal in inorganic and organic form. In addition, Se can also occur bonded with carbon [5]. The sulfidic form of Se is present in association with pyrite (FeS_2) and the selenidic form as clausthalite (PbSe) [5]. It

was possible to observe that coal samples that have higher Se concentration, such as coal “A” to “E”, showed also higher concentration of Fe (2570 to 16650 $\mu\text{g g}^{-1}$) and Pb (about 22.5 and 64.4 $\mu\text{g g}^{-1}$), that is in agreement with previous literature [5]. In addition, it was possible to observe that coal samples E, F and J have a high Br content (22.6 to 62.2 $\mu\text{g g}^{-1}$), which could cause interferences. Selenium concentrations in coal “G” to “J” and in both CRMs were below the limit of detection (LOQ) obtained by standard mode ICP-MS, indicating the necessity of developing a method with lower LOQ for Se determination in coal.

Additionally, the determination of carbon content and residual acidity on digests obtained by MAWD was performed. Carbon content and residual acidity for all samples were about 2000 mg L^{-1} and 70%, respectively. Considering the dilution factor of 10, required for the dilution of hydrofluoric acid present in digests, no interference was observed for coals “A” to “F” by ICP-MS, which is in agreement with previous work [30].

Accuracy was evaluated by spike recovery experiments. In this study, specific amounts of reference solution (150 μL of a 10 mg L^{-1} Se solution and 2.5 μL of a 10 mg L^{-1} Te solution) were added to the coal sample inside the decomposition vessel prior to the addition of the digestion solution. Spike recoveries were better than 96% for all coal samples.

3.2. CRC-ICP-MS optimization

The collision/reaction cell was designed to be positioned in the interface between the ion lens and the quadrupole mass spectrometer. This approach allows the injection of gases into the cell that cause the collapse of polyatomic ions through the physical collision and/or reaction between the gas molecule and polyatomic ions [19]. Selenium determination by ICP-MS is seriously impaired by spectral interferences due to argon-based interferences [10]. The use of CRC-ICP-MS with hydrogen gas can minimize these interferences, allowing Se to be measured at the most abundant isotopes (at m/z 80 and 78). Nowadays, the possibility of

placing the CRC in between two quadrupole mass analyzers (ICP-MS/MS) also exists, reducing even more polyatomic interferences [18].

The influence of H₂ gas flow rate used in the cell was investigated. This evaluation was carried out by monitoring the signal intensity of the four Se isotopes (⁷⁷Se, ⁷⁸Se, ⁸⁰Se and ⁸²Se) in a 10 times diluted digested coal sample at different H₂ flow rates. A blank solution prepared in 5% HNO₃ was also measured in the same way, in order to find the conditions providing the best signal to noise (S/N) ratio. Fig. 1 shows the effect of the H₂ flow rate on the S/N ratio, signal intensity and background intensity for ⁷⁷Se, ⁷⁸Se, ⁸⁰Se and ⁸²Se.

Fig. 1

The use of H₂ reduced the Ar₂ background at *m/z* 80, but the selenium signal was reduced by approximately the same extent. Consequently, the S/N ratio for ⁸⁰Se increased just by a factor of 1.87 at high H₂ flow rates, as can be observed in Fig. 1. The same behavior was observed for Se at *m/z* 82. Thus, the use of CRC-ICP-MS with H₂ was not considered an advantageous approach for these two isotopes.

It can be observed that the effect of the H₂ flow was more pronounced for Se at *m/z* 77 and 78. Better results were obtained at flow rates up to 4.8 mL min⁻¹, which increased the S/N ratio by a factor of about 30 and 40, for ⁷⁷Se and ⁷⁸Se, respectively. Therefore, the H₂ gas flow rate was kept at 4.8 mL min⁻¹ for Se determination.

Parameters of the cell can also be used when optimizing this device for the minimization of specific interferences. The rejection parameter RP_q of the cell was also adjusted. The RP_q parameter controls the low-mass cut-off regions inside the cell [39]. Organic species present in samples can decompose in plasma to their most basic components: C⁺, H⁺, and O⁺. These species enter the cell where they can react to form a variety of

hydrocarbon species at different masses [10, 11]. Adjusting the RPq value it is possible to control the chemistry inside the cell by ejecting the matrix species ions before they can react to form new interferences. In this sense, the RPq value was evaluated from 0.05 to 0.9. The best S/N ratio for the four Se isotopes evaluated in this work was by using an RPq value ranging from 0.35 to 0.45, and it was thus set at 0.45.

In addition, in order to investigate the occurrence of new polyatomic interferences caused by the reaction between concomitant matrix elements and the hydrogen gas used in the CRC, a study was performed. For that, standard solutions of Br and Ge ($5 \mu\text{g L}^{-1}$, $50 \mu\text{g L}^{-1}$ and $500 \mu\text{g L}^{-1}$) were measured in the presence of different H_2 flow rates (from 0 to 5 mL min^{-1}) in the CRC. This evaluation was carried out by monitoring the signal intensity of Se isotopes ^{77}Se , ^{78}Se , ^{80}Se and ^{82}Se . To make easy the comparison between the different H_2 flow rates, the intensity obtained for Br and Ge solutions was normalized by the intensity of a blank solution prepared in 5% HNO_3 . The effect of Br concentration was observed only for ^{80}Se and ^{82}Se isotopes, while the concentration of Ge only affected isotope ^{77}Se , as can be seen in Fig. 2.

It is possible to observe that both the interfering species and the H_2 flow rate caused an increase on the signal intensity for ^{77}Se , ^{80}Se and ^{82}Se . For Se at m/z 80 an increase of signal intensity was observed only at high concentrations of Br ($500 \mu\text{g L}^{-1}$) and at flow rates higher than 3 mL min^{-1} (Fig. 2 - A), possibly due to the formation of $^{79}\text{Br}^1\text{H}^+$. At lower H_2 flow rates the background intensity at m/z 80 was very high ($> 20,000,000$ counts) due to the formation of $^{40}\text{Ar}^{40}\text{Ar}^+$ and thus the formation of the bromine interference can not be observed. The effect of Br concentration and H_2 flow rate was more pronounced for ^{82}Se , due to the possible formation of $^{81}\text{Br}^1\text{H}^+$ a signal intensity increase was observed at lower Br concentration ($50 \mu\text{g L}^{-1}$) and at lower H_2 gas flow rate (0.5 mL min^{-1}). The signal intensity for ^{77}Se was

increased only when a solution of $500 \mu\text{g L}^{-1}$ Ge was used, which caused the formation of $^{76}\text{Ge}^1\text{H}^+$.

Fig. 2

3.3. Analytical figures of merit

After optimization of the CRC-ICP-MS method, general analytical figures of merit were evaluated. Table 3 shows the instrumental limits of detection (LOD, 3σ), which was estimated based on ten measurements of an analytical blank. Table 4 also shows the linear calibration range and the correlation coefficients (R^2) for the four Se isotopes studied in this work.

Table 4

For ^{80}Se and ^{82}Se it was not possible to calibrate at concentration lower than $0.1 \mu\text{g L}^{-1}$, since the H_2 introduced in the cell was not able to remove all argon-based interferences present at this m/z . At the same time, the use of H_2 resulted in more interferences at m/z 82. Correlation coefficients (R^2) were better than 0.999 for all Se isotopes. Relative standard deviations were lower than 6%.

The lowest limit of detection was obtained by monitoring Se at m/z 78, mainly because H_2 is able to remove efficiently $^{38}\text{Ar}^{40}\text{Ar}^+$ interfering species. In addition, the use of the CRC allowed a considerably decrease of the background intensity as well as the relative standard deviation (RSD). A comparison with the values obtained without the cell at m/z 82 (the most abundant isotope with less interference) shows that the use of the collision/reaction cell and ^{78}Se produced an improvement of about 50times of the LOD (from 0.5 to $0.01 \mu\text{g L}^{-1}$) when compared to determination without CRC system. The improvement factor is higher than the value of the isotopic ratio of $^{78}\text{Se}/^{82}\text{Se}$, so that the improvement cannot be explained only by

the ability to measure a most abundant selenium isotope, but it is also related to the interference reduction. It is important to emphasize that the LODs presented in Table 4 are instrumental LODs. Thus, the method proposed in this work monitoring Se at m/z 78 provided a method LOD of $0.01 \mu\text{g g}^{-1}$ and a method LOQ of $0.03 \mu\text{g g}^{-1}$ (250 mg of coal, 25 mL final volume, 10 times diluted).

In addition, Table 5 shows a comparison with the instrumental LODs found in the literature using other Se determination strategies. As can be seen, the LOD presented in this work compares favorably with the majority of them. In some cases, a better LOD was achieved, but by using NH_3 , CH_4 , O_2 or a mixture of He and H_2 in the cell [22, 24] and by using technologies such as HR-SF-ICP-MS and ICP-MS/MS [40-42]. In addition, only one work was found for coal [21], but the LOD was about ten times higher than that found in the present work.

Table 5

In order to evaluate the accuracy of the proposed method, the digestion of CRMs of coal (NIST 1635 and SARM 20) was performed by MAWD and Se was determined by CRC-ICP-MS under optimized conditions. Results are shown in Table 6. It was observed that the results for ^{77}Se and ^{78}Se presented no statistical difference with the certified values (t -test, 95% of confidence level) for both CRMs. However, results obtained for ^{80}Se and ^{82}Se in CRM SARM 20 were higher than the certified values. As mentioned before, the use of H_2 gas can cause other polyatomic interferences in combination with matrix elements, such as $^{79}\text{Br}^1\text{H}^+$ and $^{81}\text{Br}^1\text{H}^+$ which are not ejected from the cell by the application of the RPq value, causing an increase on the signal [39]. For ^{77}Se this increase was not observed, possibly due to the formation of $^{76}\text{Ge}^1\text{H}^+$ to be less likely to occur, once Ge is usually at low concentration in coal [1].

Table 6**3.4. Determination of Se in coal by CRC-ICP-MS**

The determination of Se was performed in other coal samples, after optimizing the conditions of the CRC-ICP-MS method. Coal samples were digested by MAWD using 250 mg of sample and a mixture of 5 mL of 14.4 mol L⁻¹ HNO₃ and 1 mL of 40% HF. Table 7 shows the concentration of Se in coal samples determined by CRC-ICP-MS and the results obtained by ICP-MS without the collision/reaction cell, monitoring the *m/z* 82.

Table 7

A statistical difference (*t*-test, 95% of confidence level) was observed between results obtained by ICP-MS without using the CRC and by monitoring ⁷⁷Se in coal “B”, “C” and “D”, ⁸⁰Se in coal “F” and ⁸²Se in coal “B”, “C”, “D”, “E” and “F”. In addition, it can be observed that the concentrations obtained monitoring ⁸²Se by CRC-ICP-MS were higher in all samples. As mentioned before, the use of H₂ in the CRC can cause other polyatomic interferences as a result of the reaction of hydrogen with matrix ions that entered the cell. A possible reason is due to the possible combination of H₂ gas with Br from the matrix forming polyatomic ions such as ⁷⁹Br¹H⁺ and ⁸¹Br¹H⁺, leading to a new polyatomic interference and higher results for these isotopes. To corroborate this hypothesis, Br content in coal samples was determined by ICP-MS after digestion by microwave-induced combustion, following previous works [37, 38] (results shown in Table 3). It was possible to see, that as higher was the bromine content in coal samples (for example, coal E, F and J) higher were the results obtained by monitoring *m/z* 82.

Additionally, elements that are usually present at high concentration in coal, such as Fe, Na, K, Ca and Si (from 100 to 20000 µg g⁻¹), could also interfere in Se determination, by

influencing in the cell. It was possible to observe that coal composition can influence the accuracy of Se determination by using isotopes 77, 80 and 82. Based on these results, it is important to highlight that a widespread use of collision/reaction technologies can produce overestimated results and also can represent a measurement with interferences if the method is not fully optimized and if the matrix concomitants are not evaluated on the method [19].

On the other hand, it can be seen that the results obtained by monitoring ^{78}Se were in good agreement with those obtained by standard mode ICP-MS using m/z 82 (t -test, 95% of confidence level) for coal samples A to F. In this sense, to avoid any possible interference, Se quantification in coal can be carried out by monitoring ^{78}Se isotope. At this m/z , no interference was observed and the LOQ was lower, making possible the determination of Se at very low concentration in coal.

4. Conclusions

It was demonstrated that the collision/reaction cell technology is a powerful tool to overcome spectral interferences at the most abundant isotopes of selenium. Hydrogen gas can effectively minimize the spectral interferences of the argon-based polyatomic ions at m/z 77, 78 and 80. However, it was possible to observe that the use of H_2 in the cell can cause polyatomic interferences with argon-, matrix- and solvent-based ions that entered the cell, which impaired Se determination using ^{77}Se , ^{80}Se and ^{82}Se . To avoid all interferences, Se determination can be carried out by monitoring ^{78}Se isotope. The instrumental LOD obtained by using the CRC with hydrogen and monitoring ^{78}Se ($0.01 \mu\text{g L}^{-1}$) was suitable for Se determination at very low concentration in coal, which was not possible using standard mode ICP-MS.

Acknowledgements

The authors are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Grant 309297/2016-8), Instituto Nacional de Ciência e Tecnologia de Bioanálítica – INCTBio (CNPq Grant Nr. 573672/2008-3) and Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS, Grants 16/2551-0000 (182-0) and 16/2551-0000516-8) for supporting this study. Funding for the sample collection provided by NERC Security of Supply programme UK (grant NE/L001764/1).

ACCEPTED MANUSCRIPT

References

- [1] F. Vejahati, Z. Xu, R. Gupta, Trace elements in coal: associations with coal and minerals and their behavior during coal utilization - a review, *Fuel* 89 (2010) 904-911.
- [2] X. Querol, J. Fernández-Turiel, A. López-Soler, Trace elements in coal and their behaviour during combustion in a large power station, *Fuel* 74 (1995) 331-343.
- [3] Z. Bian, J. Dong, S. Lei, H. Leng, S. Mu, H. Wang, The impact of disposal and treatment of coal mining wastes on environment and farmland, *Environ. Geol.* 58 (2009) 625-634.
- [4] V.V. Seredin, S. Dai, Y. Sun, I.Y. Chekryzhov, Coal deposits as promising sources of rare metals for alternative power and energy-efficient technologies, *Appl. Geochem.* 31 (2013) 1-11.
- [5] Y.E. Yudovich, M.P. Ketris, Selenium in coal: a review, *Int. J. Coal Geol.* 67 (2006) 112-126.
- [6] Annual Book of ASTM Standards. ASTM D 4606-15. Annual book of ASTM standards. Standard Test method for determination of arsenic and selenium in coal by the hydride generation/atomic absorption method, 2015.
- [7] J. Wang, T. Nakazato, K. Sakanishi, O. Yamada, H. Tao, I. Saito, Microwave digestion with HNO₃/H₂O₂ mixture at high temperatures for determination of trace elements in coal by ICP-OES and ICP-MS, *Anal. Chim. Acta* 514 (2004) 115-124.
- [8] J. Wang, T. Nakazato, K. Sakanishi, O. Yamada, H. Tao, I. Saito, Single-step microwave digestion with HNO₃ alone for determination of trace elements in coal by ICP spectrometry, *Talanta* 68 (2006) 1584-1590.
- [9] H. Lachas, R. Richaud, A.A. Herod, D.R. Dugwell, R. Kandiyoti, K.E. Jarvis, Determination of 17 trace elements in coal and ash reference materials by ICP-MS applied to milligram sample sizes, *Analyst* 124 (1999) 177-184.
- [10] E.H. Evans, J.J. Giglio, Interferences in inductively coupled plasma mass spectrometry. A review, *J. Anal. Atom. Spectrom.* 8 (1993) 1-18.
- [11] R.S. Houk, V.A. Fassel, G.D. Flesch, H.J. Svec, A.L. Gray, C.E. Taylor, Inductively coupled argon plasma as an ion source for mass spectrometric determination of trace elements, *Anal. Chem.* 52 (1980) 2283-2289.
- [12] M. Díaz-Somoano, M.A. López-Antón, M.R. Martínez-Tarazona, Determination of selenium by ICP-MS and HG-ICP-MS in coal, fly ashes and sorbents used for flue gas cleaning, *Fuel* 83 (2004) 231-235.
- [13] S.D. Tanner, Characterization of ionization and matrix suppression in inductively coupled 'cold' plasma mass spectrometry, *J. Anal. Atom. Spectrom.* 10 (1995) 905-921.
- [14] C.D. Pereira, E.E. Garcia, F.V. Silva, A.R.A. Nogueira, J.A. Nobrega, Behaviour of arsenic and selenium in an ICP-QMS with collision and reaction interface, *J. Anal. Atom. Spectrom.* 25 (2010) 1763-1768.
- [15] M. Moldovan, E.M. Krupp, A.E. Holliday, O.F.X. Donard, High resolution sector field ICP-MS and multicollector ICP-MS as tools for trace metal speciation in environmental studies: a review, *J. Anal. Atom. Spectrom.* 19 (2004) 815-822.
- [16] L. Balcaen, E. Bolea-Fernandez, M. Resano, F. Vanhaecke, Inductively coupled plasma - tandem mass spectrometry (ICP-MS/MS): a powerful and universal tool for the interference-free determination of (ultra)trace elements – a tutorial review, *Anal. Chim. Acta* 894 (2015) 7-19.
- [17] N. Jakubowski, L. Moens, F. Vanhaecke, Sector field mass spectrometers in ICP-MS, *Spectrochim. Acta Part B* 53 (1998) 1739-1763.
- [18] E. Bolea-Fernandez, L. Balcaen, M. Resano, F. Vanhaecke, Overcoming spectral overlap via inductively coupled plasma-tandem mass spectrometry (ICP-MS/MS). A tutorial review, *J. Anal. Atom. Spectrom.* 32 (2017) 1660-1679.

- [19] S.D. Tanner, V.I. Baranov, D.R. Bandura, Reaction cells and collision cells for ICP-MS: a tutorial review, *Spectrochim. Acta Part B* 57 (2002) 1361-1452.
- [20] G. Grindlay, J. Mora, M.T.C. Loos-Vollebregt, F. Vanhaecke, Evaluation of the multi-element capabilities of collision/reaction cell inductively coupled plasma-mass spectrometry in wine analysis, *Talanta* 128 (2014) 379-385.
- [21] X. Li, S. Dai, W. Zhang, T. Li, X. Zheng, W. Chen, Determination of As and Se in coal and coal combustion products using closed vessel microwave digestion and collision/reaction cell technology (CCT) of inductively coupled plasma mass spectrometry (ICP-MS), *Int. J. Coal Geol.* 124 (2014) 1-4.
- [22] J.R. Souza, L. Silva, M.S. Rocha, T.D. Saint’Pierre, Dynamic reaction cell-ICP-MS as a powerful tool for quality control of a Se-enriched dietary supplement, *Food Anal. Methods* 10 (2017) 3088–3097.
- [23] V. Dufailly, L. Noël, T. Guérin, Determination of chromium, iron and selenium in foodstuffs of animal origin by collision cell technology, inductively coupled plasma mass spectrometry (ICP-MS), after closed vessel microwave digestion, *Anal. Chim. Acta* 565 (2006) 214-221.
- [24] M. Niemelä, P. Perämäki, H. Kola, J. Piispanen, Determination of arsenic, iron and selenium in moss samples using hexapole collision cell, inductively coupled plasma-mass spectrometry, *Anal. Chim. Acta* 493 (2003) 3-12.
- [25] P. Jitaru, H. Goenaga-Infante, S. Vaslin-Reimann, P. Fisicaro, A systematic approach to the accurate quantification of selenium in serum selenoalbumin by HPLC-ICP-MS, *Anal. Chim. Acta* 657 (2010) 100-107.
- [26] N. Mketi, P.N. Nomngongo, J.C. Ngila, An innovative microwave-assisted digestion method with diluted hydrogen peroxide for rapid extraction of trace elements in coal samples followed by inductively coupled plasma-mass spectrometry, *Microchem. J.* 124 (2016) 201-208.
- [27] F.G. Antes, F.A. Duarte, M.F. Mesko, M.A.G. Nunes, V.A. Pereira, E.I. Muller, V.L. Dressler, E.M.M. Flores, Determination of toxic elements in coal by ICP-MS after digestion using microwave-induced combustion, *Talanta* 83 (2010) 364-369.
- [28] F. Low, L. Zhang, Microwave digestion for the quantification of inorganic elements in coal and coal ash using ICP-OES, *Talanta* 101 (2012) 346-352.
- [29] H. Wiltsche, M. Winkler, P. Tirk, Matrix effects of carbon and bromine in inductively coupled plasma optical emission spectrometry, *J. Anal. Atom. Spectrom.* 30 (2015) 2223-2234.
- [30] G. Grindlay, J. Mora, M. de Loos-Vollebregt, F. Vanhaecke, A systematic study on the influence of carbon on the behavior of hard-to-ionize elements in inductively coupled plasma-mass spectrometry, *Spectrochim. Acta Part B* 86 (2013) 42-49.
- [31] G. Grindlay, L. Gras, J. Mora, M.T.C. Loos-Vollebregt, Carbon-related matrix effects in inductively coupled plasma atomic emission spectrometry, *Spectrochim. Acta Part B* 63 (2008) 234-243.
- [32] E.M.M. Flores, *Microwave-assisted sample preparation for trace element determination*, Elsevier Science, Amsterdam, 2014.
- [33] K. Srogi, Microwave-assisted sample preparation of coal and coal fly ash for subsequent metal determination, *Anal. Lett.* 40 (2007) 199-232.
- [34] Z. Mester, R. Sturgeon, *Sample preparation for trace element analysis*, Elsevier, Amsterdam, 2003.
- [35] J.S.F. Pereira, R.S. Picoloto, L.S.F. Pereira, R.C.L. Guimarães, R.A. Guarnieri, E.M.M. Flores, High-efficiency microwave-assisted digestion combined to in situ ultraviolet radiation for the determination of rare earth elements by ultrasonic nebulization ICPMS in crude oils, *Anal. Chem.* 85 (2013) 11034-11040.

- [36] J.S.F. Pereira, C.L. Knorr, L.S.F. Pereira, D.P. Moraes, J.N.G. Paniz, E.M.M. Flores, G. Knapp, Evaluation of sample preparation methods for polymer digestion and trace elements determination by ICPMS and ICPOES, *J. Anal. Atom. Spectrom.* 26 (2011) 1849-1857.
- [37] E.M.M. Flores, M.F. Mesko, D.P. Moraes, J.S.F. Pereira, P.A. Mello, J.S. Barin, G. Knapp, Determination of halogens in coal after digestion using the microwave-induced combustion technique, *Anal. Chem.* 80 (2008) 1865-1870.
- [38] A.L.H. Muller, P.A. Mello, M.F. Mesko, F.A. Duarte, V.L. Dressler, E.I. Muller, E.M.M. Flores, Bromine and iodine determination in active pharmaceutical ingredients by ICP-MS, *J. Anal. Atom. Spectrom.* 27 (2012) 1889-1894.
- [39] S.D. Tanner, V.I. Baranov, A dynamic reaction cell for inductively coupled plasma mass spectrometry (ICP-DRC-MS). II. Reduction of interferences produced within the cell, *J. Am. Soc. Mass Spectrom.* 10 (1999) 1083-1094.
- [40] B.P. Jackson, A. Liba, J. Nelson, Advantages of reaction cell ICP-MS on doubly charged interferences for arsenic and selenium analysis in foods, *J. Anal. Atom. Spectrom.* 30 (2015) 1179-1183.
- [41] A.T. Townsend, The determination of arsenic and selenium in standard reference materials using sector field ICP-MS in high resolution mode, *Fresenius J. Anal. Chem.* 364 (1999) 521-526.
- [42] E. Bolea-Fernandez, L. Balcaen, M. Resano, F. Vanhaecke, Interference-free determination of ultra-trace concentrations of arsenic and selenium using methyl fluoride as a reaction gas in ICP-MS/MS, *Anal. Bioanal. Chem.* 407 (2015) 919-929.

Table 1. Selenium isotopes abundance and possible spectral interferences.

Isotope	Abundance (%)	Possible spectral interferences
^{74}Se	0.89	^{74}Ge , $^{36}\text{Ar}^{38}\text{Ar}$, $^{58}\text{Fe}^{16}\text{O}$, $^{40}\text{Ar}^{34}\text{S}$, $^{58}\text{Ni}^{16}\text{O}$, $^{39}\text{K}^{35}\text{Cl}$, $^{42}\text{Ca}^{16}\text{O}_2$
^{76}Se	9.37	^{76}Ge , $^{38}\text{Ar}^{38}\text{Ar}$, $^{36}\text{Ar}^{40}\text{Ar}$, $^{40}\text{Ar}^{35}\text{Cl}^1\text{H}$, $^{60}\text{Ni}^{16}\text{O}$, $^{40}\text{Ar}^{36}\text{S}$, $^{39}\text{K}^{37}\text{Cl}$, $^{41}\text{K}^{35}\text{Cl}$, $^{44}\text{Ca}^{16}\text{O}_2$, $^{44}\text{Ca}^{32}\text{S}$, $^{40}\text{Ca}^{36}\text{S}$, $^{64}\text{Zn}^{12}\text{C}$,
^{77}Se	7.63	$^{38}\text{Ar}_2^1\text{H}$, $^{40}\text{Ar}^{37}\text{Cl}$, $^{76}\text{Se}^1\text{H}$, $^{60}\text{Ni}^{17}\text{O}$, $^{40}\text{Ar}^{37}\text{Cl}$, $^{39}\text{K}^{38}\text{Ar}$, $^{42}\text{Ca}^{35}\text{Cl}$, $^{76}\text{Ge}^1\text{H}$
^{78}Se	23.77	$^{38}\text{Ar}^{40}\text{Ar}$, $^{40}\text{Ar}^{36}\text{Ar}^1\text{H}_2$, $^{40}\text{Ar}^{37}\text{Cl}^1\text{H}$, $^{77}\text{Se}^1\text{H}$, $^{62}\text{Ni}^{16}\text{O}$, $^{38}\text{Ar}^{40}\text{Ca}$, $^{41}\text{K}^{37}\text{Cl}$
^{80}Se	49.61	^{80}Kr , $^{40}\text{Ar}_2$, $^{40}\text{Ar}^{38}\text{Ar}^1\text{H}_2$, $^{64}\text{Zn}^{16}\text{O}$, $^{64}\text{Ni}^{16}\text{O}$, $^{40}\text{Ar}^{40}\text{Ca}$, $^{40}\text{Ar}^{40}\text{K}$, $^{48}\text{Ca}^{16}\text{O}_2$, $^{79}\text{Br}^1\text{H}$
^{82}Se	8.73	^{82}Kr , $^{40}\text{Ar}_2^1\text{H}_2$, $^{66}\text{Zn}^{16}\text{O}$, $^{68}\text{Zn}^{14}\text{N}$, $^{81}\text{Br}^1\text{H}$, $^{42}\text{Ca}^{40}\text{Ar}$, $^{34}\text{S}^{16}\text{O}_3$

ACCEPTED MANUSCRIPT

Table 2. Operational conditions for the determination of Se by ICP-MS and CRC-ICP-MS.

Parameter	ICP-MS	CRC-ICP-MS
Collision/reaction cell gas	-	H ₂
Collision/reaction cell gas flow rate, mL min ⁻¹	-	4.8
Nebulizer gas flow rate, L min ⁻¹	0.95	0.95
Auxiliary gas flow rate, L min ⁻¹	1.20	1.20
Plasma gas flow rate, L min ⁻¹	18.0	18.0
RF power, W	1300	1300
RPa	-	0
RPq	-	0.45
Sweeps/reading	5	60
Reading/replicate	3	5
Replicates	3	5
Dwell time, ms	50	50
Isotopes, <i>m/z</i> ratio	⁸² Se	⁷⁷ Se ⁷⁸ Se ⁸⁰ Se ⁸² Se

Table 3. Concentration of Br by ICP-MS after MIC, Fe by ICP-OES, Pb and Se by standard mode ICP-MS after MAWD in coal samples (mean \pm standard deviation, n = 3).

Sample	Concentration, $\mu\text{g g}^{-1}$			
	Br	Fe	Pb	Se
Coal A	16.7 \pm 0.5	16650 \pm 85	46.0 \pm 4.3	5.87 \pm 0.43
Coal B	7.19 \pm 0.32	4875 \pm 538	22.2 \pm 0.9	3.30 \pm 0.08
Coal C	7.58 \pm 0.09	4022 \pm 148	64.4 \pm 4.2	2.84 \pm 0.16
Coal D	3.51 \pm 0.05	1812 \pm 114	21.9 \pm 0.7	2.41 \pm 0.09
Coal E	22.6 \pm 0.1	2570 \pm 70	22.5 \pm 0.2	2.15 \pm 0.08
Coal F	54.9 \pm 0.4	1815 \pm 12	12.5 \pm 0.1	1.63 \pm 0.14
Coal G	9.34 \pm 0.08	1066 \pm 60	3.78 \pm 0.11	< 1.5*
Coal H	16.5 \pm 0.3	744 \pm 19	3.32 \pm 0.01	< 1.5*
Coal I	2.18 \pm 0.05	1904 \pm 174	9.31 \pm 0.54	< 1.5*
Coal J	62.2 \pm 1.1	986 \pm 6	1.40 \pm 0.01	< 1.5*
NIST 1635**	nd	nd	nd	< 1.5*
SARM 20**	nd	nd	nd	< 1.5*

*LOQ obtained by ICP-MS considering a dilution factor of 10 times.

**Certified values for NIST 1635: 0.9 \pm 0.3 and SARM 20: 0.8 (0.7 - 1.0)

nd: not determined

Table 4. Calibration range and limit of detection obtained by CRC-ICP-MS for Se determination.

Isotope	Calibration range, $\mu\text{g L}^{-1}$	Correlation coefficient	LOD, $\mu\text{g L}^{-1}$
^{77}Se	0.05 – 10	0.999807	0.03
^{78}Se	0.05 – 10	0.999982	0.01
^{80}Se	0.1 – 10	0.999987	0.07
^{82}Se	0.1 – 10	0.999791	0.3
^{82}Se (standard mode)	1 – 10	0.999754	0.5

ACCEPTED MANUSCRIPT

Table 5. Comparison of the LODs reported in the literature for Se determination by ICP-MS using collision and/or reaction cells.

Species monitored	System ^a (gas)	LOD	Sample	Reference
⁷⁸ Se	CCT (H ₂ /He)	0.095 µg L ⁻¹	Coal and coal combustion products	[21]
⁸⁰ Se	CCT (H ₂ /He)	0.41 µg L ^{-1b}	Foodstuffs of animal origin	[23]
⁸⁰ Se	CCT (H ₂ /He)	0.029 µg L ⁻¹	Moss samples	[24]
⁸⁰ Se	DRC (CH ₄)	0.01 µg kg ^{-1c}	Yeast samples	[22]
⁹⁶ SeO	DRC (O ₂)	0.03 µg kg ^{-1c}	Yeast samples	[22]
⁸⁰ Se	DRC (O ₂)	0.06 µg kg ^{-1c}	Yeast samples	[22]
⁸⁰ Se	DRC (NH ₃)	0.1 µg kg ^{-1c}	Yeast samples	[22]
⁹⁶ SeO	MS/MS (O ₂ /H ₂)	0.003 µg L ⁻¹	Food products	[40]
⁹⁴ SeO	MS/MS(O ₂ /H ₂)	0.002 µg L ⁻¹	Food products	[40]
⁸⁰ Se	MS/MS (CH ₃ F/He)	0.004 µg L ⁻¹	Apple leaves, rice flour, fish and sediment	[42]
⁸² Se	HR-SF	0.0005 µg g ^{-1c}	Water, tomato leaves, oyster tissue, river sediment and urine	[41]
⁷⁸ Se	CRC (H ₂)	0.01 µg L ⁻¹	Coal	This work

^a CCT: collision cell technology; CRC: collision/reaction cell; DRC: dynamic reaction cell; MS/MS: triple quadrupole; HR-SF: high resolution sector field.

^b LOQ

^c data from this reference are not provided to calculate the instrumental LOD.

Table 6. Results for Se by CRC-ICP-MS in coal CRM (mean \pm standard deviation, n = 3).

Isotope	Se concentration, $\mu\text{g g}^{-1}$	
	NIST 1635	SARM 20
^{77}Se	0.973 ± 0.027	1.02 ± 0.06
^{78}Se	0.929 ± 0.037	0.869 ± 0.028
^{80}Se	1.10 ± 0.09	1.16 ± 0.07
^{82}Se	1.25 ± 0.13	1.75 ± 0.33
Certified value	0.9 ± 0.3	$0.8 (0.7 - 1.0)^*$

*Confidence level

Table 7. Results for Se ($\mu\text{g g}^{-1}$) by ICP-MS and CRC-ICP-MS in coal samples after digestion by MAWD (mean \pm standard deviation, n = 3).

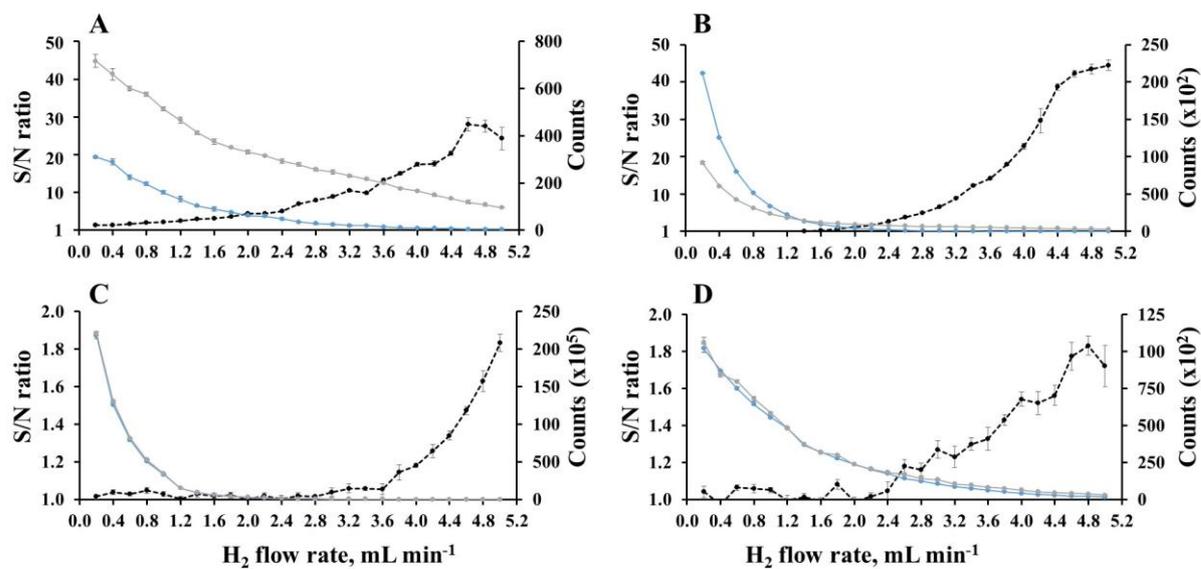
Sample	CRC-ICP-MS				ICP-MS*
	^{77}Se	^{78}Se	^{80}Se	^{82}Se	^{82}Se
Coal A	5.62 \pm 0.41	5.31 \pm 0.54	5.26 \pm 0.40	6.46 \pm 0.31	5.87 \pm 0.43
Coal B	4.43 \pm 0.35	3.59 \pm 0.36	3.97 \pm 0.27	4.60 \pm 0.36	3.30 \pm 0.08
Coal C	3.25 \pm 0.18	2.85 \pm 0.14	2.90 \pm 0.17	3.87 \pm 0.11	2.84 \pm 0.16
Coal D	2.99 \pm 0.14	2.60 \pm 0.13	2.55 \pm 0.09	3.00 \pm 0.10	2.41 \pm 0.09
Coal E	1.90 \pm 0.22	2.15 \pm 0.27	1.66 \pm 0.19	4.25 \pm 0.30	2.15 \pm 0.08
Coal F	1.88 \pm 0.06	1.73 \pm 0.07	2.80 \pm 0.14	7.52 \pm 0.66	1.63 \pm 0.14
Coal G	2.15 \pm 0.01	0.723 \pm 0.054	1.05 \pm 0.02	2.13 \pm 0.06	< 1.5**
Coal H	1.21 \pm 0.12	0.717 \pm 0.036	1.26 \pm 0.10	3.04 \pm 0.30	< 1.5**
Coal I	0.642 \pm 0.060	0.452 \pm 0.027	0.595 \pm 0.026	0.88 \pm 0.05	< 1.5**
Coal J	0.579 \pm 0.053	0.289 \pm 0.017	1.87 \pm 0.20	7.58 \pm 0.86	< 1.5**

* Determination by ICP-MS using standard mode.

** LOQ obtained by ICP-MS considering a dilution factor of 10 times.

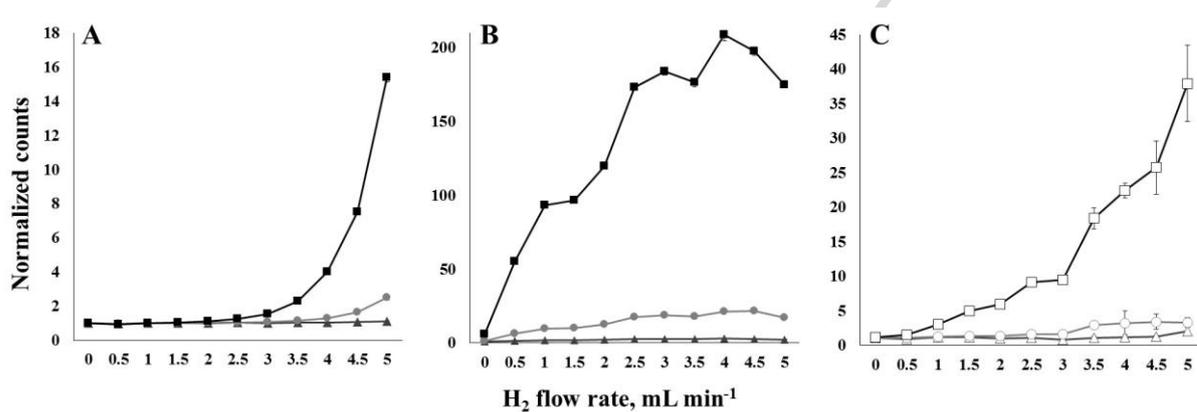
Figure caption

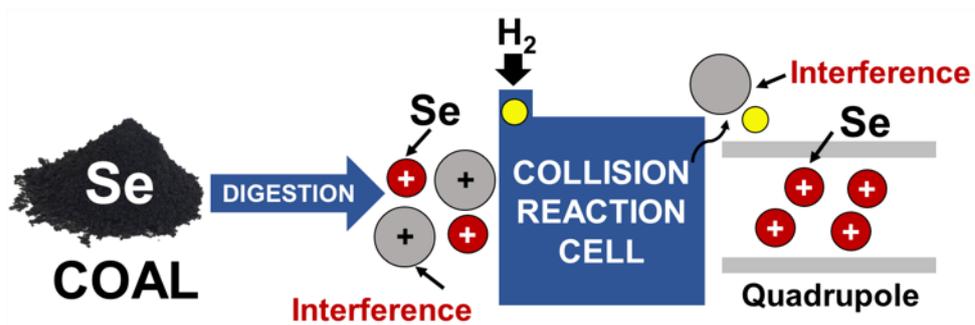
Fig. 1. Effect of H₂ gas flow rate on the Se signal to noise (S/N) ratio (---), signal intensity (—) and background (—), for (A) ⁷⁷Se, (B) ⁷⁸Se, (C) ⁸⁰Se and (D) ⁸²Se isotopes. Error bars are the standard deviation (n = 3).



ACCEPTED

Fig. 2. Effect of H_2 gas flow rate, Br and Ge concentration on the signal intensity of (A) ^{80}Se , (B) ^{82}Se and (C) ^{77}Se , for $5\ \mu\text{g L}^{-1}$ Br (\blacktriangle), $50\ \mu\text{g L}^{-1}$ Br (\bullet), $500\ \mu\text{g L}^{-1}$ Br (\blacksquare), $5\ \mu\text{g L}^{-1}$ Ge (\blacktriangleleft), $50\ \mu\text{g L}^{-1}$ Ge (\circ) and $500\ \mu\text{g L}^{-1}$ Ge (\square). Error bars are the standard deviation ($n = 3$).





Graphical abstract

ACCEPTED MANUSCRIPT

Highlights

- ✓ Selenium was determined at low level in coal by CRC-ICP-MS.
- ✓ Hydrogen was feasible to minimize the argon-based interferences at m/z 77, 78, 80 and 82.
- ✓ The limit of detection was 50 times better than that obtained using the standard mode ICP-MS.

ACCEPTED MANUSCRIPT