DETERMINATION OF SELENIUM BY ICP-MS AND HG-ICP-MS IN COAL, FLY ASHES AND SORBENTS USED FOR FLUE GAS CLEANING

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ABSTRACT

Selenium is an element of environmental concern which content in coal is generally lower than 2 mg g^{-1}. During coal utilization for power generation this element may be emitted in gas phase or condensed in the particulate matter. To avoid the problems originated by such emissions different systems are being developed to retain selenium compounds in the system using solid sorbents. In this work, the determination of selenium in a variety of solid materials related with the use of coal for energy production was evaluated by two methods; ICP-MS and HG-ICP-MS. Coals, fly ashes and various solids used as sorbents in gas cleaning processes (kaolin, limestone, alumina, metal oxide mixtures and activated carbons), were the materials analyzed. In some of these materials, selenium can be determined with similar results by either method. However in coal, fly ashes and some activated carbons, the use of a HG-ICP-MS is necessary to avoid interferences. The results obtained by both methods in samples whose selenium content ranges from µg g^{-1} to mg g^{-1}, are discussed. In general, good (± 2-4%) to excellent (± 1-2%) agreement between the reference and the obtained concentrations was achieved in the analysis of certified and reference samples. The precision of the analysis, including instrumental, sample preparation and sample homogeneity uncertainties was evaluated, the relative standard deviation (RSD) being lower than 10% in all cases.

KEYWORDS: selenium determination, microwave digestion, ICP-MS, HG-ICP-MS, coal, fly ashes, solid sorbents.

INTRODUCTION

Selenium is one of the most volatile trace elements of environmental concern present in coal, its content commonly ranging between 0.2 and 1.4 μg g^{-1} [1]. During coal combustion and gasification, selenium compounds evaporate or condense on the smallest fly ash particles, and are emitted with flue gases into the environment in different proportions. Various methods are under study to reduce these emissions, retention on solid sorbents being one of the most promising**.** Clay minerals, limestone, fly ashes and metal oxide mixtures are being tested as sorbents for gas cleaning at high temperatures (between 350 and 750ºC) [2-4], whereas activated carbons are being examined for the capture of selenium at the lowest (<200ºC) [5]. Maximum retention capacities in these materials range between 1 and 60 mg g^{-1} depending not only on the characteristics of the sorbent but also on sorption conditions [6]. The successful development and setting up of a gas cleaning process implies monitoring the quantity of selenium retained. Moreover, the correct evaluation of the selenium content in the coal and of that retained in the ashes and sorbents will make it possible to estimate the levels of selenium finally emitted into the environment. Consequently, a sensitive and accurate method for selenium analysis in coal, coal ashes and sorbents is required.

Before choosing an adequate method, three important points should be borne in mind. One is the wide range of selenium concentrations in the different samples to be analysed ranging from µg g^{-1} to mg g^{-1}. The second is the different characteristics of the samples. In one site, some of the sorbents are 100 % m/m mineral matter containing more than 75 % m/m of silica while in other activated carbons contain more than 75 % m/m of organic matter. Between these two extremes some samples such as coals, are made up of both organic and mineral matter in different proportions. The third consideration concerns the different modes of occurrence of selenium in the samples. Although in most cases selenium will be present in the form of a HNO_3 soluble compound (adsorbed selenium, or selenium sulphides), exceptionally it may also be present in clays [1] or as a glassy solution in fly ashes. In order to analyse these heterogeneous materials, dissolution methods, capable of dissolving selenium in a variety of samples, and precise and accurate methods for selenium determination, are necessary.

A number of fast and efficient acid decomposition procedures, which make use of microwave ovens have already been published for coal, ashes and geological samples [6-12]. In this work, two methods were developed. One of them was applied to kaolin, limestone, alumina, fly ashes, and metal oxides, all of which were mixed with sand as in the sorption experiments, while the other was applied to coals and activated carbons.

The analysis of selenium in solution can be carried out by different procedures. AAS hydride generation is the most widely used for low concentrations [13-15], but ICP-MS may also give good results with the important advantage that it is a multielemental technique [7-12, 16]. Using ICP-MS, a simultaneous analysis of other volatile trace elements retained in the sorbents, can be carried out. Moreover, this sensitive method can also be used for relatively high concentrations. However, the use of ICP-MS for the determination of selenium has its limitations. Selenium is weakly ionised in argon plasma and most of the six selenium isotopes (^{74}Se 0.89%; ^{76}Se 9.36%; ^{77}Se 7.63%; ^{78}Se 23.78%; ^{80}Se 49.61% y ^{82}Se 8.73%), undergo significant isobaric or polyatomic interferences, the most important being Ar_2 in 76, 78 and 80 masses. ArCl interference is possible in chlorine matrices when ^{77}Se is used while ^{82}Se, the most suitable isotope for selenium quantification, suffers BrH interference in matrices containing Br. Because the relative proportions of chlorine and bromine in the samples studied in this work are low, the selenium analysis was checked using the less abundant isotopes ^{77}Se and ^{82}Se. However the presence, in some of the samples, of elements such as Zn, Sm and Dy, that form Sm^{2+}, Dy $^{2+}$ and Zn-O in the plasma, interfered with the determination of the ^{77}Se and ^{82}Se isotopes. Another collateral problem in the analysis of some of the samples studied was their relatively high sulphur content, which forms H_2SO_4, in the acidic solution, causing deterioration of the Ni and Cu interfaces in the equipment. To avoid these problems, the hydride generation method coupled with the ICP-MS technique (HG-ICP-MS) [17-19] was used and compared with the direct ICP-MS method.

EXPERIMENTAL

The materials used as sorbents at high temperature were: kaolin (K), limestone (L), coal fly ashes (FA), γ-alumina (A), and the metal oxide mixtures containing spinels; Zn_2TiO_4 (ZT), and $ZnFe_2O_4$ (ZF). The ZT and ZF samples were prepared by calcination of mixtures of commercial ZnO, Fe_2O_3 and TiO_2 at 1100ºC. All these sorbents were used in sorption experiments [8] and were mixed with sand in the proportion of 1+3, sorbent+sand. Before digestion they were thoroughly homogenised and ground in a Retsch Spectro Mill. The activated carbons used for gas cleaning at low temperature were Norit. RBHG3 and Norit. RB3. RBHG3 contains about 6 % m/m of a sulphur compound.

Five reference materials of similar characteristics to the sorbents were used in this work. The high-selenium content reference sample (ASe) and the activated carbon reference samples (ACSe1 and ACSe2), were not standard samples and were prepared specifically for this study. These reference samples were necessary because of the lack of standard samples with similar characteristics to the inorganic sorbents with high selenium concentrations, and because there are no standard activated carbons with certified selenium contents. The reference materials were obtained by adding a known amount of selenium to finely ground alumina (ASe) and to the activated carbons RBHG3 (ACSe1) and RB3 (ACSe2) by dropping a solution of a selenium salt in such a way that the quantity of solution is the exact amount necessary to fill the porous structure of the material. The concentration of selenium in solution was calculated so as to obtain 0.75 mg of selenium per g of sample in ASe and 17.3 and 19.5 μg of selenium per g of sample in ACSe1 and ACSe2 respectively. After impregnation, the sample was dried at a temperature lower than 40ºC. The standard samples, were the certified NIST SRM coal fly ash 1633a (10.3 μg g^{-1} of selenium) and the NIST SARM-20 coal (0.8 μg g^{-1} of selenium). To include all the possible variables in the uncertainty of the results the reference materials ASe and SRM 1633a were mixed and homogenised with sand in the same proportion as the sorbents are used in some retention experiments [6], and the mixture was ground before dissolution and analysis. The coal and the activated carbons were just ground.

Sample digestion was carried out in a microwave oven (Milestone MLS 1200) fitted with an EMS exhaust unit and a microprocessor to control the power. Teflon high-pressure digestion vessels (HPV80) were used. Six vessels were placed in the oven simultaneously.

Sample dissolution was carried out in a different way for the samples enriched in inorganic and organic matter. For inorganic materials and minerals about 0.100 g of sample was digested. Because the size of the sample to be dissolved is of critical importance, digestion with different particle sizes was tested. It was found that the best results were obtained by grinding the sorbent+sand mixture to a size close to 50 µm. An acid mixture capable of completely dissolving all sorbents containing silica was selected after testing, its composition being 2 ml of HNO_3 65%, 4 ml of HF 40% and 5 ml of saturated H_3BO_3. Boric acid was added after dissolution to neutralise the corrosive hydrofluoric. The digestion program is described in Table 1.

Table 1.- Instrumental parameters for the determination of selenium by ICP-MS

Inductively Coupled Plasma		***Mass spectrometer***	
RF Power	1200 w	Sampling cone	Ni
Carrier Gas	1.27 l min^{-1}	Skimmer cone	Ni
Plasma Gas	15.0 l min^{-1}	Data acquisition	3 points per mass
Auxiliary Gas	1.0 l min^{-1}	Integration time	0.10 s per point
Sample Depth	5.6 mm	Acquisitions	5
Peri-pump	0.1 rpm	Isotopes measured	^{82} Se and ^{103} Rh
Nebuliser	Babington		

The selenium present in the coal and the retained in the activated carbons was extracted by using 7.5 ml of suprapur HNO_3 65%, which was added to 50 mg of sample (ground to 50 µm) in closed Teflon vessels. The microwave program consisted in subjecting the sample to a power of 600 w for 6 min. After the vessels were cooled, the samples were filtered.

Table 2- Instrumental parameters for the determination of selenium by HG-ICP-MS.

Hydride generator	
$NaBH_4$	1% / NaOH
Acid Concentration	HCl 1.6M
Inductively Coupled Plasma	
RF Power	1200 w
Carrier Gas	1.20 l min^{-1}
Plasma Gas	15.0 l min^{-1}
Auxiliary Gas	0.60 l min^{-1}
Sample Depth	5.6 mm
Mass spectrometer (As described in Table 1)	

The analysis of selenium in solution was carried out by ICP-MS and HG-ICP-MS. The ICP-MS equipment was an HP 4500 and the operating parameters used are listed in Tables 2 and 3. Instrumental conditions were optimised using a tune solution containing 10 ppb of ^{7}Li, ^{89}Y, ^{140}Ce and ^{205}Tl. The solution obtained by the microwave dissolution method was diluted to 50 ml. For ICP-MS conventional analysis, an aliquot (between 100 and 500 µl) of this solution and 100 µl of a 1 µg ml^{-1} solution of the internal standard (^{103}Rh) were taken to 10 ml. The internal standard was used in order to compensate the instrumental drift while standard additions were used to compensate matrix interferences. In another hand, to determine selenium by HG-ICP-MS, and to obtain the necessary acidity for the formation of the hydride, 1.5 ml of HCl 30% was added to an aliquot of 8.5 ml of the solution from the microwave digestion, resulting a final volume of 10 ml. In this case 10 ppb of rhodium were added too, in order to compensate the signal drift. The spray chamber was used as gas-liquid separator.[17] The system set-up consisted in connecting the sample and the reducing agent ($NaBH_4$) with a Y-type connector and rotating the nebulizer (babintong) 180º (Figure 1). The mixed solution was introduced into the nebuliser, and the hydride formed was transferred into the plasma to be ionised. Conditions for hydride generation were optimised and selenium determination was optimised to the indicated in Table 3.

Table 3.- Microwave digestion program for samples containing silica.

Stage 1: HNO_3 + HF	
Time (min)	*Power (w)*
8	300
4	600
5	450
5	Vent.
Stage 2: H_3BO_3	
Time (min)	*Power (w)*
6	600
3	Vent.

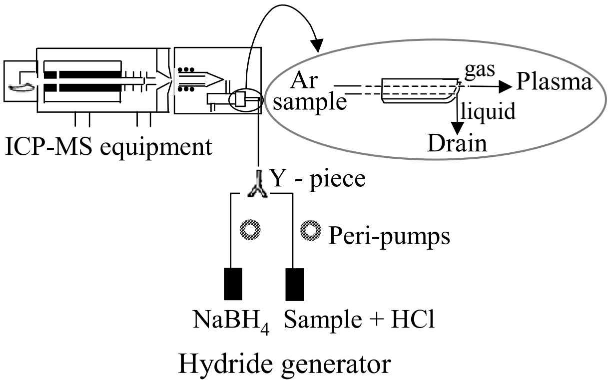

Figure 1. Diagram of the HG-ICP-MS system.

RESULTS AND DISCUSSION

For conventional ICP-MS, the quantification method was selected from results obtained for the analysis by external calibration and standard additions of solutions with a known concentration of selenium (10 ppb) in the different matrices. In this way, matrix effects for various matrices, that were compensate with the standard addition method, were observed. Plotting the slope ratio of the lines obtained for acid calibration (Ac) and standard additions (Ad) the presence of these matrix effects could be corroborated (Figure 2). The slope ratios obtained for the different matrices are quite different from 1, ranged between 0.6 and 0.8. By HG-ICP-MS the hydride formed is separated (95% efficiency for the system used) from the sample so matrix effects are minimised and external calibration is an appropriate quantification method for selenium determination.

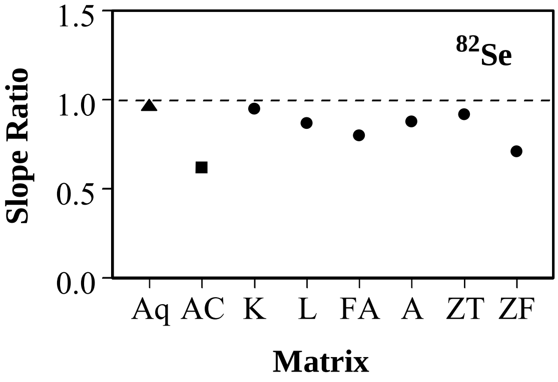

Figure 2.- Ratios between the slopes obtained by external calibration with acid and aqueous solutions (▲) and between the slopes obtained by standard addition and calibration in the problem solution (■). AC; Activated Carbon; K; Kaolin, L; Limestone, F.A.; Fly Ashes, A; Alumina, ZT and ZF; metal oxide mixtures).

The reference and standard materials were employed throughout the work to provide data quality assurance. After a preliminary study in which the determination of selenium was evaluated comparatively, using ^{77}Se and ^{82}Se in the samples, ^{82}Se was chosen for the analysis. It was not possible to analyse the certified standards 1633a and SARM 20 by ICP-MS, because of their complex matrix and high zinc content (220 µg g^{-1} and 17 µg g^{-1} respectively), the Zn/Se ratio being close to 21 in both cases. The reference sample ASe, whose selenium content is in the order of mg g^{-1}, and the ACSe2, whose selenium content is in the order of µg g^{-1}, were used to validate the method. All the reference materials and standard samples were analysed by HG-ICP-MS.

The accuracy and precision of the results obtained were evaluated. As can be seen (Tables 4-5) good (± 2-4%) to excellent (± 1-2%) agreement was achieved between the certified or reference values and those obtained by the methods studied. The

Table 4.- Results of selenium determination by ICP-MS in reference samples

ICP-MS		
Parameter	*ASe (mg g^{-1})*	*ACSe2 (µg g^{-1})*
n	11	11
SD_{Total}	0.08	0.76
SD_{Instr}	0.04	0.58
SD_{SP}	0.07	0.49
$X_{reference}$	0.75	19.5
$\overline{X}$	0.77	19.1
% RSD	10.4	4.0

n; number of replicates, SD_{tot}; standard deviation of the analysis, SD_{int}; standard deviation of the instrument, SD_{sp}; standard deviation of sample preparation, $X_{reference}$, certified or added concentration, $\overline{X}$; average value, %RSD; relative standard deviation.

Table 5 **.-** Results of selenium determination by HG-ICP-MS in reference samples

HG-ICP-MS					
Parameter	*µg g^{-1}*				*mg g^{-1}*
	ACSe1	*ACSe2*	*SARM 20*	*1633a*	*ASe*
SD_{Total}	1.45	1.33	0.08	0.96	0.07
$SD_{Inst.}$	0.96	0.92	0.06	0.60	0.02
SD_{SP}	1.09	0.96	0.05	0.75	0.06
$X_{reference}$	17.3	19.5	0.80	10.3	0.75
$\overline{X}$	17.0	18.7	0.83	10.1	0.71
% RSD	9.06	6.68	9.64	9.50	9.86

precision of the analysis was considered as being due to two independent sources of error, the uncertainty in the sample preparation procedure and instrumental precision. Calculations are based on equation (1) [14], in which SD_{SP} is the uncertainty in the sample preparation procedure; SD_{Total} analytical precision and SD_{Instr} instrumental precision.

$$(SD_{Total})^2 = (SD_{SP})^2 + (SD_{Instr})^2 \qquad (1)$$

SD_{Total} was evaluated by analysing fifteen replicate samples of the mentioned reference materials. Then averages x, standard deviations SD and relative standard deviations (%RSD) were calculated. Repeatability of instrumental measurements (SD_{Instr}) was tested by analysing one of the above mentioned solutions fifteen times. Tables 5-6 give the values of these parameters for the standard and reference samples. It should be borne in mind that in the reference material (not certified standards), the uncertainty of the results also includes the homogeneity of the incipient wetness procedure used to impregnate the solid with selenium.

Table 4 shows the results of the analysis of selenium by direct ICP-MS for the samples ASe and ACSe2, in which the elements that may produce interferences are minimum. In these samples, results obtained were statistically indistinguishable from the reference values with absolute error ranging between 2-3% and an RSD of 10 and 4 % respectively.

The results obtained by HG-ICP-MS for all the reference materials are given in Table 5. In all cases relative standard deviations are lower than 10% for 15 replicates, and the differences between the reference or certified values and the results obtained were below 5%. It can be observed (Tables 4-5) that the sample preparation uncertainty obtained in the analysis is similar to instrumental uncertainty, a similar contribution being made in all cases to total uncertainty. In general, the values obtained for the instrumental uncertainty by HG-ICP-MS are higher than those obtained by ICP-MS due to the instability observed in the argon plasma as a result of hydrogen excess produced during hydride generation.

Uncertainty was also estimated by using samples with different unknown concentrations of selenium. The samples analysed were sorbents obtained after performing sorption experiments in which conditions varied, as a consequence of which the concentration in each sample was different. Table 6 shows the results obtained from each sample as the average of 5 determinations. Generally speaking, standard deviation does not depend on the nature of the sample analysed and relative standard deviations for 5 determinations are lower than 16% in most cases. The uncertainty of the results is due not only to the uncertainty of the analytical method, determined by the reference materials (Tables 4-5), but also to the variations in the retention experiment and the unhomogeneity of the sorbent bed.

Table 6.- Average values obtained for n=5 replicates in samples of sorbents containing different quantities of selenium after sorption experiments.

Sample	***mg Se g^{-1}***	***SD***	***RSD***	***Sample***	***mg Se g^{-1}***	***SD***	***RSD***
K(1)	4.04	0.66	16.0	A(1)	1.10	0.18	16.4
K(2)	5.62	0.35	6.23	A(2)	1.28	0.14	10.9
K(3)	6.06	0.97	16.0	A(3)	1.09	0.12	11.0
L(1)	50.7	4.28	8.44	ZT(1)	39.7	2.18	5.49
L(2)	43.0	5.33	12.0	ZT(2)	59.9	2.24	3.74
L(3)	65.9	4.88	7.40	ZT(3)	58.4	3.13	5.36
FA(1)	25.0	3.10	12.4	ZFT(1)	21.8	3.99	18.3
FA(2)	25.8	3.72	14.4	ZFT(2)	37.7	3.85	10.2
FA(3)	25.4	1.77	6.97	ZFT(3)	54.3	6.24	11.5

K; Kaolin, L; Limestone, FA; Fly ashes, A; Alumina and ZT and ZF; metal oxide mixtures (all mixed with sand).

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