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Optimisation of flow-injection-hydride generation inductively coupled plasma spectrometric determination of selenium in electrolytic manganese

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Abstract

Flow-injection-hydride generation procedure for Se in electrolytic manganese was optimized by means of the experimental design approach. Instrumental variables like power supplied (P), sample (F) and argon (G) flow rates together with chemical variables like $NaBH_4$ and HCl concentrations were studied. In case of the chemical variables, it was concluded that sodium tetrahydridoborate concentrations higher than 1.0% extinguished the plasma while HCl concentration should always be higher than $0.6\,mol\,dm^{-3}$. The analysis of effects suggested that all the instrumental variables are significant factors, and the optimum conditions were $P = 1550\,W$, $F = 4.75\,mL\,min^{-1}$ and $G = 0.6\,mL\,min^{-1}$. The influence of Mn was specially studied and it was concluded that the interferences were negligible if Mn is below $2.0\,g\,L^{-1}$. In the same sense, the interferences of antimony(III), arsenic(V) and mercury(II) were also considered negligible. Finally, a detection limit of 0.0005% (w/w) was obtained (a repeatability R.S.D. <2.0% for all Se concentrations tried). Some manganese samples were also spiked with different concentrations of Se(IV) and the results demonstrated to be in good statistical agreement with expected values.

Keywords: Selenium determination; Electrolytic manganese; Hydride generation; Inductively coupled plasma; Variables optimisation; Aluminium alloying

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1. Introduction

Manganese is essential to metallurgical industries (aluminium and steel foundries) with important applications. Manganese additions in aluminium are required for food and drinking packings, domestic tools, decoration or covering. Manganese used for aluminium alloys is produced by electrolysis wherein selenium additions are purposefully added to improve the electrical current efficient [1]. This leads to the contamination of manganese as a result of co-deposition of selenium at the cathode. It is believed that over 90% of the selenium used for improving the current efficiency of the electro-winning of electrolytic manganese enters the cathode in the elemental form and, thus, some of the electrolytic grade of manganese currently used can contain variable quantities of selenium (0.03–0.16%) [2].

Within the operating aluminium furnaces (700–800 °C), selenium is supposed to evaporate out of the molten aluminium as metal vapour. Therefore, as a consequence of toxicity and environmental hazard in high concentrations of selenium and its compounds [3,4], furnace stack emissions and occupational airborne exposures must be monitored. In that sense, total selenium concentration in aluminium alloying process, raw and waste materials must be also controlled to identify the Se environmental fate and exposures in aluminium processing. Hagelstein [2] studied the environ-

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mental management of selenium in aluminium processing and indicated that the main environmental issues were selenium particulates in emissions and drosses produced in operating aluminium furnaces. The aluminium and steel industries may limit their future environmental liabilities due to selenium accumulation in processing facilities and waste streams by avoiding or controlling raw material inputs containing selenium. Thus, different confident selenium analyses should be developed for implementation in cast-houses and metallurgical industries [5,6].

Great selectivity and sensibility are obtained in aqueous samples by using different atomic techniques as inductively coupled plasma optical emission spectrometry (ICP–OES), ETAAS or AFS. Besides, the implementation of cold vapour or hydride generation previous to electrothermal atomic absorption detection increases this selectivity minimising spectral interference caused by other matrix component [7]. In the last decade, on-line flow-injection (FI) separation techniques have become increasingly popular for the determination of trace elements in different kind of sample [8].

Hydride generation (HG) together with inductively coupled plasma optical emission spectrometry (ICP–OES) is a widely used method for the determination of selenium [9–10]. However, there is lack of information in the literature on this procedure for Se determination in electrolytic manganese. This analytical technique (FI–HG–ICP–OES) enables separation of selenium from the major components of the sample but, in fact, is prone to interference from several transition metal ions and other volatile elements. The transition metal interference occurs in the liquid phase and leads to a significant inhibition of selenium signal. Specifically, manganese ions present in the sample solution in hydride generation conditions yield manganese borides, which absorb hydrides and cause their decomposition [11]. Manganese species may catalyse decay of reducing agent as well. This chemical interference is well documented in a review article by Nakahara and Kikui [12]. However, the treatment of mutual interference by hydride-forming elements is relatively scarce and only few works discuss the possible interference mechanism [13,14]. Therefore, the study and the identification of the different factors or variables influencing the hydride generation procedure is clearly required in order to establish a correct analytical method for selenium determination.

As a consequence, the main purpose of the present study is to find the optimal set of operational conditions that allow a simple and sensitive method for the determination of Se in electrolytic manganese by FI–HG–ICP–OES. The experimental approach to accomplish this aim was the experimental design [15]. As it is already known, experimental design is the most powerful way to make efficient experiments as we get the information we need with the minimum effort. In this sense, a full factorial design was used to screen the effect of each variable while a composite design was used to build the response surface.

2. Experimental

2.1. Reagents and solutions

Calibration solutions of every trace element considered were prepared using ICP standard solutions (1000 mg L^{-1}) from Merck (Darmstadt, Germany) in manganese presence (2 g L^{-1}). All solutions were prepared using analytical grade HCl from Merck (Darmstadt, Germany) and de-ionised water. HNO_3 from Merck (Darmstadt, Germany) was also used.

$NaBH_4$ (1%, w/v) and NaOH (0.1 mol dm^{-3}) from Merck (Darmstadt, Germany) were used as reagents in the hydride generation.

2.2. Instrumentation

An inductively coupled plasma optical emission spectrometer IRIS advantage (Thermo Corporation) with a CID detector was used. The instrument consists on a multi-channel peristaltic pump and gas–liquid separator assembled to the spectrometer (T-PHD). A 196.090 nm line for Se was used and no background correction system was used. The presence of spectral interference was considered negligible when the contribution of the interfering signal at the selenium wavelength was less than 10% [16,17].

Detailed operating conditions for plasma excitation and hydride generation are listed in Table 1.

2.3. Digestion of electrolytic manganese

Electrolytic manganese (Xiangxi Autonomous Prefecture, China) was collected in flakes and crushed into a laboratory mill (Retsch S100) and sieved (500 μm). An acid digestion of the manganese powder obtained (2 g) was immediately performed using concentrated HCl without heating [18]. This procedure was performed both with a water cooling (refrigerant) and without it. Similar efficiency (signals) was obtained for all samples in both procedures (Fig. 1). Thus, analytical determination of Se(IV) was independent on the use of a cooling column in the digestion step.

Table 1
Optimum operating conditions for FI–HG–ICP–OES experiments

Supplied power (*P*)	1550 W
Plasma Ar flow rate	2.0 L min^{-1}
Auxiliary Ar flow rate	0.5 L min^{-1}
Carrier Ar flow rate (*G*)	0.6 mL min^{-1}
Pressure on nebuliser	28 psi
Se wavelength	196.090 nm
Integration time	60 s
Background correction	Yes (IRIS/AP)
Sample flow rate (*P*)	180 rpm or 4.75 mL min^{-1}
$NaBH_4$ flow rate (*P*)	180 rpm or 4.75 mL min^{-1}
$NaBH_4$ concentration	1.0% in NaOH 0.1 mol dm^{-3}
Samples acidity	HCl: 0.6 mol dm^{-3}

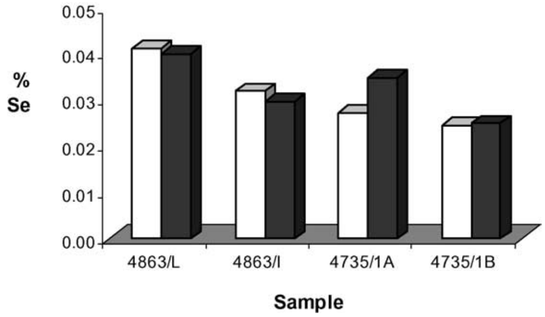

Fig. 1. Se concentration obtained with (☐) and (■) without cooling column.

2.4. Thermodynamic selenium speciation

The two common inorganic oxidation states of selenium are IV and VI, but only the lower state (IV) is successfully reduced to hydrogen selenide by $NaBH_4$ [19]. Thus, it is important to verify that the main species of Se after HCl digestion is IV state.

This fact has been both thermodynamically and experimentally confirmed (Fig. 2a and b). Fig. 2a shows the distribution diagram of Se against pH while Fig. 2b shows the predominance diagram of Se against pH and redox potential, using the MEDUSA program [20]. In both cases, all aqueous species described in the literature were taken into account to solve the chemical equilibria [21,22]. As can be seen, when the aqueous solutions are alkaline or the redox potential is high, the predominance Se(VI) species should be considered. Therefore, the use of HNO_3 has to be avoided during the digestion of Mn, while HCl assures the dissolution of Mn and Se, in such conditions, is present as Se(IV) species.

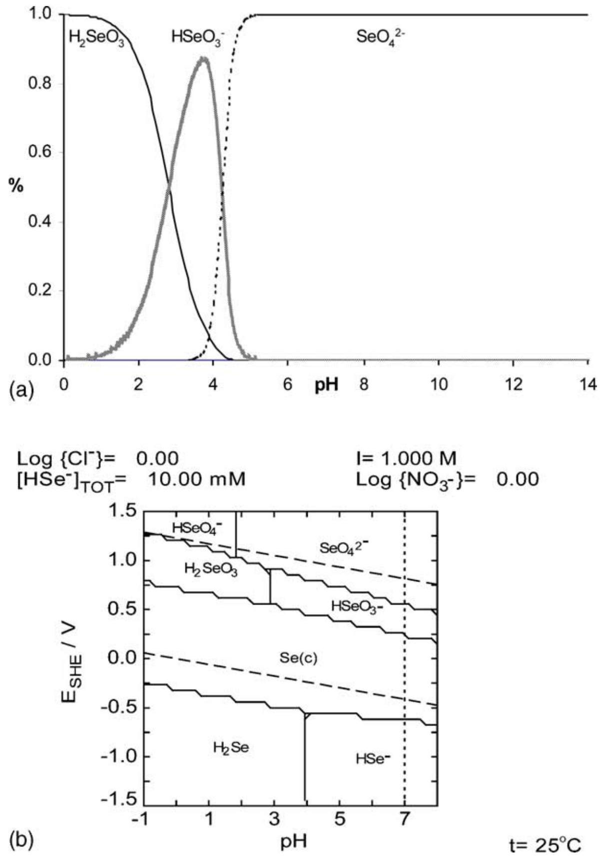

Fig. 2. Distribution diagram of Se against pH (a) and predominance diagram of Se (800 μg L^{-1}) (b).

2.5. Hydride generation procedure

For selenium hydride generation, the sample (in HCl 0.6 mol dm^{-3}) and sodium tetrahydridoborate (1.0%) solutions are introduced into the FI system using a peristaltic pump. The solutions are then pumped through a gas–liquid separator in a continuous stream. The released hydrides are supported by the carrier gas flow (Ar flow rate of 0.6 mL min^{-1}) to the plasma. The reading time is 30 s and no background correction is used.

3. Results and discussion

The efficiency of selenide generation depends directly on the $NaBH_4$ concentration. However, $NaBH_4$ concentrations higher than 1.1% destabilised the plasma discharge due to excessive hydrogen evolution and concentrations higher than 2.0% extinguished the plasma. Thus, $NaBH_4$ concentration of 1.0% was considered the highest operating value in all the analysis performed and it was kept constant.

Hydrochloric acid has been found to be the most satisfactory medium to generate hydrides. The efficiency of selenide generation was constant at HCl concentrations above 1 mol dm^{-3} (Fig. 3). However, higher HCl concentrations than 1 mol dm^{-3} produce several deleterious effects: a decrease in pump winding life, an increase in acid fume problems and an increase in the violence of by-product hydrogen gas evolution. The efficiency of hydride generation increased slightly with the increasing HCl concentration or reached a plateau above 0.6 mol dm^{-3}. Lower concentration values (HCl <0.4 mol dm^{-3}) were enough to produce complete inhibition in the selenium reduction.

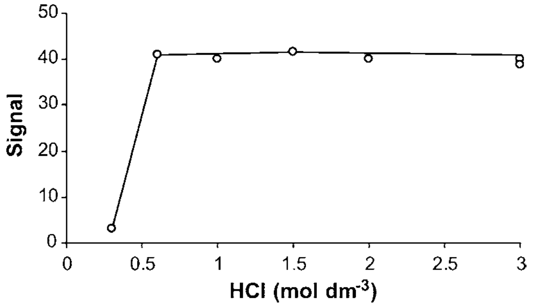

Fig. 3. Influence of HCl concentration on Se response in 2 g L^{-1} Mn.

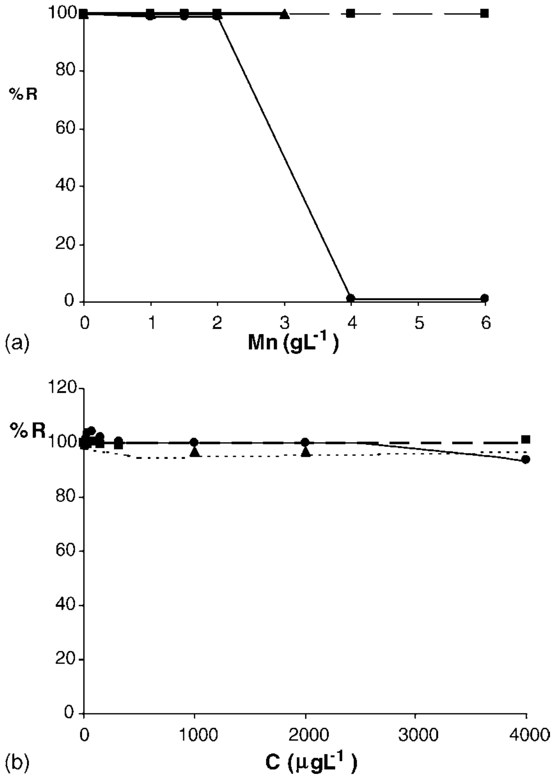

Fig. 4. (a) Influence of manganese on the selenium determination at different HCl concentrations: (●—●) 0.6 mol dm^{-3}, (▲—▲) 1.5 mol dm^{-3} and (■—■) 3.0 mol dm^{-3}. (b) Influence of hydride-forming elements on the selenium response: (●—●) As(V), (▲—▲) Hg(II) and (■—■) Sb(III).

Effect of the presence of electrolytic manganese on the selenium determination (Se: 200 µg L^{-1}) was also examined for concentrations ranged from 0 to 6.0 g L^{-1} Mn.

The hydride generation efficiency (%R) was defined as:

$$\%R = \frac{S_{Sei}}{S_{Seo}} \times 100 \qquad (1)$$

where S_{Sei} is the intensity of Se obtained with interferences and S_{Seo} is the intensity of Se with interferences.

In general, manganese had a negative effect on the selenium response at concentrations higher than 2 g L−1 (Fig. 4a). This inhibition could be overcome increasing the HCl concentration but two assumptions were taken into account to fix optimum HCl concentration at 0.6 mol dm−3: low HCl concentrations are less drastic and inexpensive, and Mn concentrations higher than 2 g L−1 were not expected.

Finally, interference from other hydride forming elements like Sb(III), As(V), Hg(II) on the determination of Se(IV) were systematically investigated. It has been shown in the literature [14] that hydride generation interference does not depend on the analyte-to-interferent ratio but on the interfering concentration in the solution for measurement. The relative sensitivities (%R), i.e. the ratio of the signal obtained with different concentrations of As(V), Sb(III) or Hg(II) and without those interferences, are depicted in Fig. 4b. Only when concentration levels of As(V) are high (2 mg L^{-1}), a decreasing Se signal was observed. Therefore, influence of those volatile elements on the selenium response was not considered in this case.

Reaction rates for hydride generation are controlled by several interdependent variables: (I) the concentration of $NaBH_4$ as reducing agent, (II) the acid concentration of the sample, (III) the chemical form of the hydride-forming element and (IV) the oxidation state of the hydride-forming element. On the one hand, as mentioned above, $NaBH_4$ and HCl concentrations were not included in the optimisation due to the experimental limitations. On the other hand, Se(IV) is the main oxidation state in solutions obtained from HCl digestion of electrolytic manganese. Therefore, only instrumental variables of the FI–HG–ICP–OES determination of Se were studied using aqueous standard solutions and electrolytic manganese powder spiked with 48 and 80 µg L^{-1} of Se(IV).

3.1. Optimisation of selenium detection: factorial design

Several variables such as: power supplied (P), sample flow rates (F), and auxiliary Ar flow rate (G) could affect the selenide detection. In order to find the main factors affecting the detection procedure, a two-level full factorial design ($2^3 + 4$ replicates of central point) was carried out using ‘The Unscrambler’ program (Camo, As. Norway, v.7.5) [23]. Table 2 lists the experimental design matrix and the response obtained (intensity, mean of three determinations). The analysis of the effects was carried out with ‘The Unscrambler’ program, and it was concluded that all the variables shown a significant effect on the response (p level <0.05), particularly G and P.

3.2. Orthogonal central composite design (CCD)

Since all the variables were significant, the design was extended to a central composite design. In this way, it is possible to build the response surface and to obtain the instrumental conditions that define the maximum response. The CCD designs developed were carried out using ‘The Unscrambler’ program. Table 3 shows the central composite design together

Table 2
Experimentation proposed and results obtained by the full factorial design

Exp	F (rpm)	G (mL min^{-1})	P (W)	Intensity (196.090 nm)
(−, −, −)	140	0.6	1150	58.99
(+, −, −)	180	0.6	1150	75.52
(−, +, −)	140	1.0	1150	17.78
(+, +, −)	180	1.0	1150	23.95
(−, −, +)	140	0.6	1550	81.72
(+, −, +)	180	0.6	1550	103.8
(−, +, +)	140	1.0	1550	59.53
(+, +, +)	180	1.0	1550	71.68
(0, 0, 0)	160	0.8	1550	52.42
(0, 0, 0)	160	0.8	1350	52.18
(0, 0, 0)	160	0.8	1350	52.18
(0, 0, 0)	160	0.8	1350	51.95

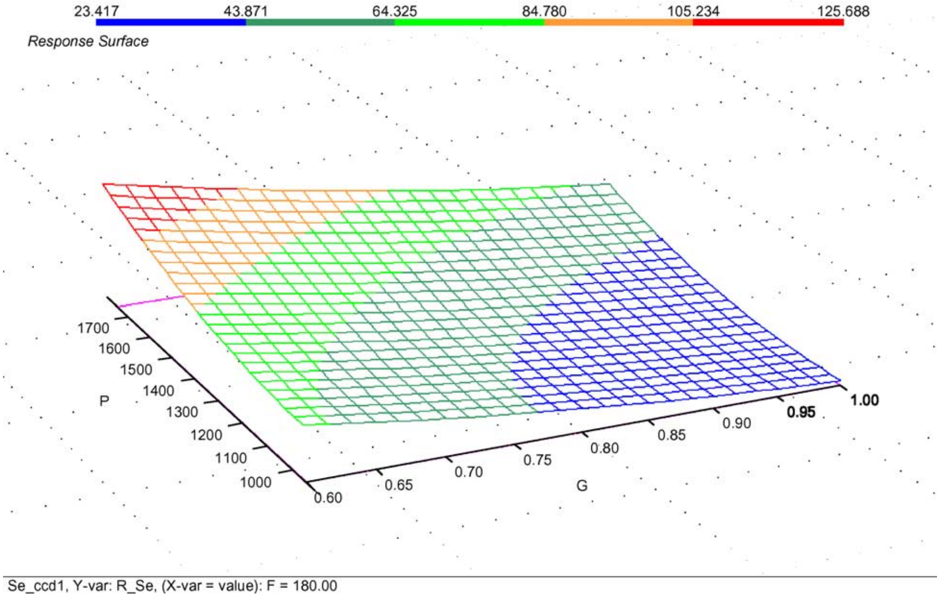

Fig. 5. Response surface obtained for optimisation of selenium determination.

with the response obtained. The response surface was calculated with ‘The Unscrambler’, and the significant effect of *G* and *P* variables was reassured, while *F* and P^2 were significant at $p = 0.07$ and $p = 0.052$, respectively.

If the *F* variable is fixed at the maximum level of the CCD (180 rpm or 4.75 mL min^{-1}), it is possible to plot the response surface as a function of the most significative variables, as can be seen in Fig. 5. From that plot we can deduce the optimum conditions within the factor space, i.e. without any extrapolation. As a consequence, the determination of Se can be carried out with a power of (*P*) 1550 W and an Ar flow rate of (*G*) 0.6 mL min^{-1}.

As there are no certified reference materials for Se(IV) in electrolytic manganese, synthetic Se(IV) tests solutions prepared in our laboratory and different real samples spiked with 48 and 80 μg L^{-1} of Se(IV) were used to check the accuracy of the analytical method (Table 4). As it can be seen, the matrix effect is negligible because the Se concentrations obtained are identical in both direct and spiked determination. Finally, the detection limit, defined as blank signal + 3 S.D., where S.D. is the standard deviation of five measurements of a blank, was estimated as 0.0005%. The precision of the method (R.S.D.) for five replicate measurements is lower than 2.0% for all concentrations tried.

Table 3
Experimentation proposed and results obtained by CCD

Exp	*G* (mL min^{-1})	*F* (rpm)	*P* (W)	Intensity (196.090 nm)
(−, −, −)	0.7	150	1150	43.18
(+, −, −)	0.9	150	1150	21.06
(−, +, −)	0.7	170	1150	49.27
(+, +, −)	0.9	170	1150	23.83
(−, −, +)	0.7	150	1550	68.34
(+, −, +)	0.9	150	1550	40.80
(−, +, +)	0.7	170	1550	78.73
(+, +, +)	0.9	170	1550	47.91
$(-\alpha_a, 0, 0)$	0.6	160	1350	76.06
$(+\alpha_a, 0, 0)$	1.0	160	1350	34.18
$(0, -\alpha_b, 0)$	0.8	140	1350	41.55
$(0, -\alpha_b, 0)$	0.8	180	1350	55.01
$(0, 0, -\alpha_c)$	0.8	160	950	47.62
$(0, 0, +\alpha_c)$	0.8	160	1750	75.93
(0, 0, 0)	0.8	160	1350	47.81
(0, 0, 0)	0.8	160	1350	47.81
(0, 0, 0)	0.8	160	1350	47.55
(0, 0, 0)	0.8	160	1350	47.35

Table 4
Se concentration in electrolytic manganese obtained by FI–HG–ICP–OES system

Sample identification	C_{Se} (%)
4853[a]	<d.l.[d]
4788/5[a]	0.026
4853[b]	<d.l.[d]
4788/5[b]	0.028
4853[c]	<d.l.[d]
4788/5[c]	0.028

[a] Se content obtained by direct FI–HG–ICP–OES.
[b] Corrected Se content after spiking with 48 μg L^{-1} Se(IV).
[c] Corrected Se content after spiking with 80 μg L^{-1} Se(IV).
[d] d.l. = 0.0005%.

4. Conclusions

The use of experimental designs shows that the three variables studied (power supplied, Ar flow rate and pump flow rate) are significant in inorganic selenium determination. Sodium tetrahydridoborate and hydrochloric acid are important variables too. However, they were not optimise because higher values than 1.0% for $NaBH_4$ and 0.6 mol dm^{-3}

for HCl extinguished the plasma. No more critical variables were found for the hydride generation of selenium.

Under the optimum conditions found ($P = 1550\,\mathrm{W}$, $F = 180\,\mathrm{rpm}$ or $4.75\,\mathrm{mL\,min^{-1}}$, and $G = 0.6\,\mathrm{mL\,min^{-1}}$), the developed method shows adequate analytical performance for the direct selenium determination in electrolytic manganese.

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