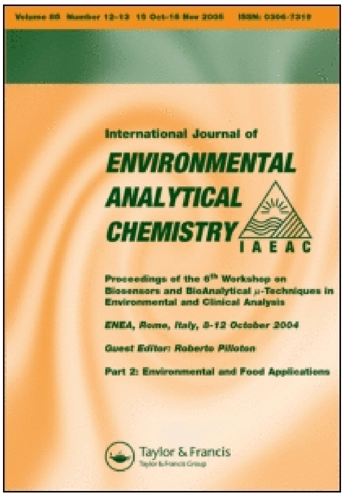

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Investigation of electrochemical hydride generation coupled to microwave plasma torch optical emission spectrometry for the determination of arsenic: analytical figures of merit, interference studies and applications to environmentally relevant samples

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Investigation of electrochemical hydride generation coupled to microwave plasma torch optical emission spectrometry for the determination of arsenic: analytical figures of merit, interference studies and applications to environmentally relevant samples

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A continuous flow thin layer electrolysis cell with a Pt cathode in combination with a microwave plasma torch operated with Ar as working gas was used for the optical emission spectrometric determination of As with the hydride technique. Under the optimised conditions the limit of detection (3σ) in the case of the As(I) 228.81 nm emission line was 81 ng mL^{-1}. Especially the influence of the transition metals Cu(II), Fe(III) and Ni(II), of the hydride forming elements Sb(III), Se(IV) and Sn(II) and of Na on the determination of As was studied. Cu(II) was found to be the strongest interferent, as in the presence of 100 $\mu\text{g mL}^{-1}$ of Cu(II) the signal for 3 $\mu\text{g mL}^{-1}$ of As was reduced to 4% of the signal without interferent. Sn(II) and Sb(III) were found to yield an increase of the signal for As. L-cysteine and KI/ascorbic acid (1 : 1) at a concentration of 2% were found effective to reduce the interferences of Cu(II), Fe(III) and Ni(II). For a solution containing 3 $\mu\text{g mL}^{-1}$ of As and 100 $\mu\text{g mL}^{-1}$ of Ni(II) it was shown that in the presence of L-cysteine or KI/ascorbic acid the signal for As was 99% and 94% of the one without interferent, whereas it was only 43% without masking reagents. The procedure could be used for the determination of As in a digested coal fly ash standard reference material (NIST SRM 1633a®) with a certified value of $145 \pm 15\,\mu\text{g g}^{-1}$ for As. A concentration of $131 \pm 15\,\mu\text{g g}^{-1}$ was found. Additionally, As could be determined in two process water samples from a copper refinery. It was found that the amount of As determined with ECHG-MPT-OES agrees well with the values determined by FAAS and ICP-OES at the 0.02 and 1.6 g L^{-1} level, respectively.

Keywords: arsenic; microwave plasma torch; electrochemical hydride generation; optical emission spectrometry; interferences; masking reagents

1. Introduction

Chemical hydride generation (CHG) employing $NaBH_4$ as a reductant is widely used for the determination of volatile hydride forming elements such as As by optical emission spectrometry (OES) using various plasma sources. A serious drawback of the technique is the chemical interferences in the liquid phase caused by the transition and noble metals

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ions [1,2]. It is assumed that the interfering ions are reduced to metals or metalboride species that form finely dispersed particles, which adsorb the hydrides thus promoting their decomposition [3]. Furthermore, the interfering ions might contribute to the decomposition of the reducing reagent. On the contrary mutual interferences from other volatile hydride forming elements were found to be not so drastic [2,4]. Usually, by the use of masking reagents, like L-cysteine, thiourea and KI the interferences caused by some transition and noble metals in the determination of As can be decreased considerably [1,4,5].

Nowadays electrochemical hydride generation (ECHG) is known to be a good alternative to CHG, especially as the interferences by concomitants were found to be less severe [6]. It was also shown that in combination with plasma spectrometry ECHG can offer lower limits of detection than CHG for the determination of As [7]. An additional advantage of the ECHG as compared to CHG lies in the fact that the use of NaOH and $NaBH_4$ can be avoided, thus saving operation costs and eliminating a potential source of contamination [8]. In an electrolysis cell the formation of hydrides takes place at the surface of the cathode in the cathode compartment, which is separated from the anode compartment by a cation exchange membrane. The latter prevents the diffusion of both anolyte and catholyte and enables a transport of electric current between the electrodes.

The ECHG was recognised as a suitable sample introduction technique for microwave induced plasmas (MIP), which are less expensive but powerful alternatives to ICP-OES as a result of their low power and gas consumption. Indeed ECHG could already be successfully used in combination with the microwave plasma torch (MPT), the surfatron and the TE101 resonator [6,7,9].

The MPT is a very robust, cheap and easy to use radiation source for OES and it can be operated with Ar, He, N_2 and even with air as working gas [10]. It was originally developed by Jin and colleagues [11], who first introduced it at the Pittsburgh Conference in 1985, and then it was further improved by Jin and colleagues [12]. Özmen and colleagues [7] previously compared the use of CHG with ECHG using different electrolysis cells for the determination of As by means of MPT-OES. It was found that the detection limit for As obtained with a cell comparable to that introduced by Lin and colleagues [13] is lower than that obtained with CHG. For a miniaturised electrolysis cell with an internal volume of 1.2 mL, as it was used formerly by Bings and colleagues [14], it could be shown that the interferences of ECHG caused by Ca, Cu and Fe are lower than in CHG.

The interferences observed in ECHG can be separated into three groups: (1) interferences caused by transition metal ions that can be electrolytically reduced to finely dispersed metals which contribute to a decomposition of the hydrides at their surface; (2) interferences due to strong oxidants which can change the oxidation state of the analyte or cause a depolarisation of the electrode; and (3) interferences caused by other hydride forming elements which can be deposited on the electrode and change the efficiency of the ECHG [8]. Interferences of heavy metals in HG are known to change, for example as a result of the addition of a series of complexing agents. Ding and colleagues [15], for example, have investigated the influence of thiourea and L-cysteine on the interferences caused by Cu in the case of the determination of Sb by flow injection ECHG coupled to graphite furnace atomic absorption spectrometry. Here an auxiliary Ar purge gas was admitted to the cathode compartment of the electrolysis cell in order to facilitate a rapid separation of SbH_3 from the liquid phase. The addition of 5% L-cysteine (w : v) or 1% thiourea (w : v) in $1\,mol\,L^{-1}$ HCl showed no decrease of the interference for a determination of Sb in the presence of $100\,\mu g\,mL^{-1}$ of Cu.

In the present work the interferences of various metal ions in the determination of As in ECHG-MPT-OES were determined. Ar was used as working gas, because it is the cheapest of the noble gases. The analytical performance of the procedure in terms of the limit of detection, the precision, the linear dynamic range and the susceptibility to interferences caused by transition metal ions, hydride forming elements and Na in the determination of As were assessed. Furthermore, the influence of L-cysteine and KI/ascorbic acid (1 : 1) as masking reagents on the interferences from Cu(II), Fe(III) and Ni(II) in the determination of As will be reported. It will be shown that the procedure can be used for the determination of As in environmentally relevant samples, such as a certified coal fly ash sample (NIST SRM 1633a®) and process water samples from a copper refinery industry. As comparative methods flame atomic absorption spectrometry and inductively coupled plasma optical emission spectrometry were used for the analysis of the process water samples.

2. Experimental

2.1 *Microwave plasma torch*

For the present work an in-house made MPT, similar to the one described by Pack and colleagues [10] was used with Ar as working gas. The microwave energy at a frequency of 2.45 GHz is produced in a magnetron and is coupled into the plasma via an antenna. The discharge was initiated by a short-circuit between the intermediate and the central tube with a steel rod. To minimise the emission of microwave radiation, the MPT was placed inside a housing made of Cu. The plasma was viewed side-on and the emitted radiation was focused with a lens to the entrance slit of a Czerny-Turner monochromator (Triax550®, HORIBA Jobin Yvon, Munich, Germany). Details on the instrumentation are given in Table 1.

2.2 *Electrolysis cell*

For all measurements an in-house made thin-layer electrolytic flow cell, comparable to the one described by Lin and colleagues [13] was used. This cell consists of two polytetrafluorethylene (PTFE) rings and two PTFE discs. The rings enclose the anode and the cathode compartments and have respective inlets and outlets for solutions.

Table 1. Details of instrumentation.

MPT	In-house made tunable microwave plasma torch according to [10]
Microwave generator	Magnetron, 2.45 GHz, 55–450 W (Erbe Elektromedizin)
Lens	Quartz, $f = 100$ mm
Monochromator	0.55 m Czerny–Turner mounting, grating constant: $a = 1/1200$, entrance slit width: 40 μm, exit slit width: 70 μm (Horiba Jobin–Yvon)
Photomultiplier	R928® (Hamamatsu)
Power supply for the ECHG	Digi 40® (Voltcraft)
Peristaltic pump	Perimax 12® (Spetec)

The compartments are separated by a Nafion® cation-exchange membrane, which prevents diffusion of the anolyte and the catholyte but enables electrical current to flow between the Pt electrodes having each a diameter of 3.5 cm. The internal volumes of the cathode and the anode compartments are 2 and 10 cm^3, respectively. The cell is held together with six screws and can easily be demounted so as to remove contamination or memory effects. For the thin-layer electrolytic flow cell used in the present study, Pt was selected as a cathode material because of its lower susceptibility to interferences from transition metal ions in comparison to vitreous carbon or Pb [8]. The acidified sample as well as the anolyte were continuously pumped at the same rate into the cell with the aid of a two channel peristaltic pump. The anolyte was not recirculated so as to prevent from any leakage due to pressure build-up.

2.3 *Reagents and solutions*

All chemicals used were of analytical grade. Standard solutions of As were daily prepared by diluting a 1 $g L^{-1}$ As(III) stock solution (single-element standard®, CPI International, Amsterdam, The Netherlands) with H_2SO_4 (96%, Merck p.a., Darmstadt, Germany) and doubly distilled water. Aqueous solutions of the interferents Cu(II), Fe(III), Na and Ni(II) were prepared from solids ($CuSO_4$, $Fe_2(SO_4)_3$, Na_2CO_3 and $Ni(NO_3)_2$) while the solutions of Sb(III), Se(IV) and Sn(II) were prepared from aqueous standard solutions (AAS-Standards Titrisol®, Merck, Darmstadt, Germany).

The influence of the masking reagents L-cysteine and KI/ascorbic acid (1 : 1) on the interferences caused by 50 and 100 $\mu g mL^{-1}$ of Cu(II), Fe(III) and Ni(II), respectively, was investigated by adding the masking reagents and the interfering ions to synthetic solutions containing 3 $\mu g mL^{-1}$ of As(III). After a dilution with 0.75 $mol L^{-1}$ H_2SO_4 to a volume of 50 mL, the resulting solutions were stored for 2 h before use so as to enable the formation of complexes.

2.4 *Sample preparation and analysis*

The analytical features of the ECHG-MPT-OES procedure developed were investigated through the determination of As in a coal fly ash standard reference material (NIST 1633a®, Gaithersburg, USA) and by its application to the analysis of two process waters stemming from a copper refinery. The coal fly ash was dried for 5 h at 110°C and afterwards 200 mg of the sample were weighed into PTFE-digestion vessels (XP-1500 Plus®, CEM) followed by an addition of 3 mL of 30% (m/v) H_2O_2 (Merck p.a., Darmstadt, Germany), 3 mL of subboiled concentrated HNO_3 (69%, Merck p.a., Darmstadt, Germany) and 4 mL of H_2SO_4 (96%, Merck p.a., Darmstadt, Germany). The digestion was performed using a microwave assisted digestion system (Mars 5®, CEM, Kamp-Lintfort, Germany). After digestion HNO_3 was evaporated from the sample solutions by heating them on a hot plate until white fumes appeared. Subsequently, 1 g of L-cysteine was added and the solutions were diluted to 50 mL with water. To prevent any potential clogging of the cell, the partially digested sample solutions were filtered through dense filter papers. Two H_2SO_4-containing process water samples from a copper refinery were diluted with a 0.75 $mol L^{-1}$ H_2SO_4 solution to a final volume of 50 mL. Afterwards, L-cysteine was added to reach a respective concentration of 2% (w : v). In all experiments calibration by standard addition was performed.

In addition, As was determined in the two process water samples by means of ICP-OES (Spectro Ciros CCD®, Spectro, Kleve, Germany) and – as the concentrations to be determined were high enough – also by FAAS (SOLAAR S4®, Thermo, Dreieich, Germany).

The concentrations of the interferents Cu(II), Fe(III), Ni(II), Na, Sb(III), Se(IV) and Sn(II) in the process water samples were determined by FAAS using calibration with synthetic standard solutions.

To determine the efficiency of ECHG the exiting solution at the drain of the cathode compartment was collected and the concentration of the remaining As was determined by FAAS. The efficiency R is calculated as $100\%((As_0 - As_D)/As_0)$ where As_0 and As_D are the concentrations of As in the initial and in the drain solution, respectively. Further, the volume of H_2 produced in the electrolysis cell was determined by inserting the outlet tube from the cathode compartment directly into a graduated cylinder filled with water.

3. Results and discussion

3.1 *Optimisation of MPT-OES*

A univariant optimisation of the microwave power, the working gas flow and the carrier gas flow for the MPT-OES was performed with respect to the net intensity for the As(I) 228.81 nm line, which was found to provide for the highest SBR as compared to other As lines. The influence of the above mentioned working parameters is shown in Figures 1, 2 and 3 and the optimised working parameters as well as the working ranges are listed in Table 2.

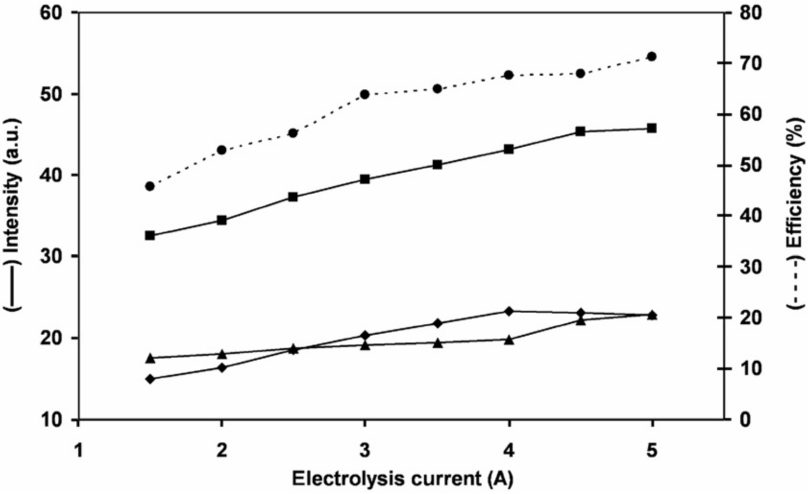

Figure 1. Effect of the electrolysis current on the total intensity (■), the net intensity (♦), the intensity of the spectral background (▲) for the As(I) 228.81 nm line and on the efficiency of hydride generation of the ECHG (●).

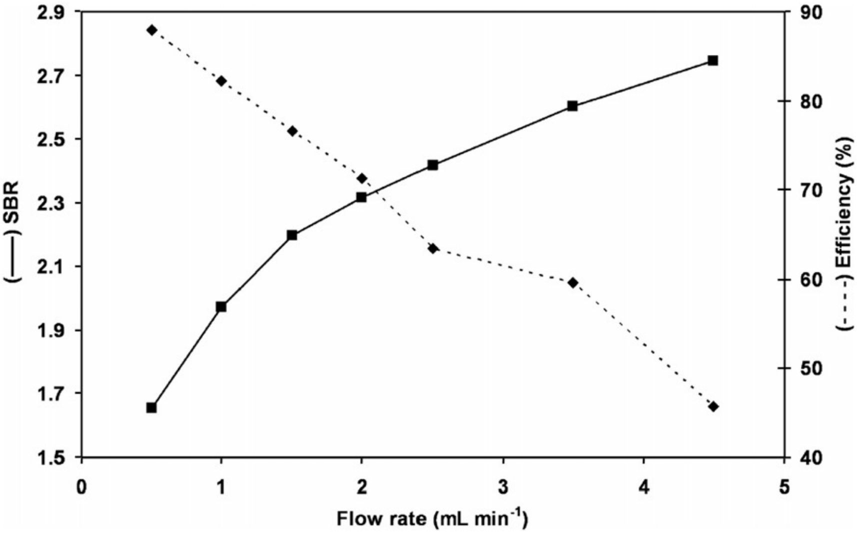

Figure 2. Effect of the flow rate on the SBR for the As(I) 228.81 nm emission line (■) and on the efficiency of the ECHG (◆).

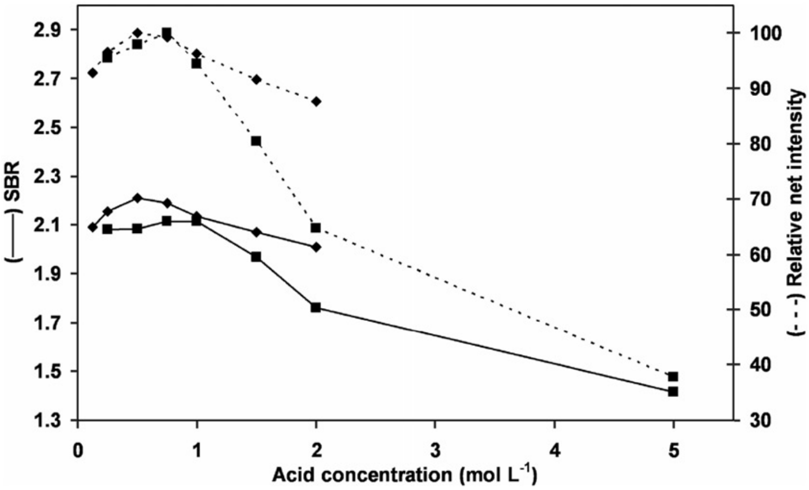

Figure 3. Effect of the concentration of H_2SO_4 in the catholyte (■) and the anolyte (◆) on the SBR and on the relative net intensity for the As(I) 228.81 nm emission line.

3.2 *Optimisation of the electrochemical hydride generation*

3.2.1 *Electrolysis current*

As shown in Figure 1, it was found that the total intensity of the As(I) 228.81 nm line increases with the electrolysis current. This can be understood from the higher generation efficiency for the volatile hydrides of As, which increases from 46 to 71% when the electrolysis current changes from 1.5 to 5 A. The net intensity of the As(I)

Table 2. Investigated ranges and optimum values of the working parameters with respect to the net intensity for the determination of As by ECHG-MPT-OES.

	Working range	Optimal value
MPT-OES		
Microwave power (W)	65–145	110
Working gas flow rate (mL min^{-1})	600–2000	1600
Carrier gas flow rate (mL min^{-1})	0–300	100
ECHG		
Electrolysis current (A)	1.5–5	4
Concentration of H_2SO_4 in catholyte (mol L^{-1})	0.25–5	0.75
Concentration of H_2SO_4 in anolyte (mol L^{-1})	0.12–2	0.5
Flow rate of catholyte and anolyte (mL min^{-1})	0.5–4.5	2.5

228.81 nm line was found to increase until the current reaches 4 A after which it decreases. As the intensity of the background increases more than the net intensity of the As line the dependance of the SBR on the current follows a similar trend and its optimum was found to be at 4 A.

Further experiments showed that the amount of H_2 produced in the cathode compartment linearly increases with the electrolysis current. When changing the current from 1 to 5 A, the volume of H_2 increases from 7.5 mL min^{-1} to 39 mL min^{-1}. It can be assumed that the introduction of higher amounts of H_2, however, results in an increased background intensity and a deterioration of the SBR.

3.2.2 *Flow rate of the catholyte and the anolyte*

It was found that the SBR for the As(I) 228.81 nm line increases with the flow rates of the catholyte, which might be due to a higher throughput of As and a higher generation rate for AsH_3. This is shown in Figure 2, in which also the efficiency of the ECHG is represented. The latter was found to decrease with the flow rate of the catholyte. For flow rates of 0.5 and 4.5 mL min^{-1}, an efficiency of 88 and 46%, respectively, was found.

3.2.3 *H_2SO_4 concentration in the catholyte and the anolyte*

Figure 3 shows that the influence of the concentration of H_2SO_4 in the anolyte on the SBR and the net intensity is rather low.

However, the acid concentration in the catholyte showed to have a stronger influence on the SBR. Accordingly, it can be assumed that the concentration of H_2SO_4 in the catholyte especially influences the diffusion of the analyte to the cathode and in consequence the efficiency of the ECHG [16–18].

3.3 *Analytical figures of merit*

Under the optimised ECHG parameters, a stable MPT discharge could be achieved, and the limit of detection for As was found to be 81 ng mL^{-1}. It was calculated by dividing three times the standard deviation of the blank through the slope of the calibration curve.

The precision in terms of the relative standard deviation was found to be 2% for 10 measurements in the case of a solution containing 3 $\mu g\,mL^{-1}$ of As. It was found that the linear dynamic range of the calibration curve for As extended from the detection limit to 15 $\mu g\,mL^{-1}$.

The higher detection limit obtained in this study in comparison to that formerly obtained by Özmen and colleagues [7] could be related to the use of Pt as cathode material. This is known to have a lower efficiency in the production of arsine than vitreous carbon [19]. The choice of Pt in this study was made, however, because it is known to have a lower susceptibility to interferences from metal ions [8].

3.4 *Interferences from transition metals, hydride forming elements and sodium*

Previous studies have demonstrated that the ECHG of As is prone to interferences from transition metal ions and hydride forming elements such as Cu(II), Fe(III), Ni(II), Na, Sb(III), Se(IV) and Sn(II). To study these effects in detail, each of these potential interferents were added at different concentrations to a solution containing 3 $\mu g\,mL^{-1}$ of As. The relative net intensity for As was obtained by rationing the net intensity for As for a solution containing the interferent and the net intensity for As obtained for an interferent-free solution.

As can be seen in Figure 4 the presence of each of the transition metals Cu(II), Fe(III), Ni(II) causes a decrease of the relative net intensity for As, whereas Cu(II) was found to be the strongest interferent. On the contrary Sb(III) and Sn(II) were found to increase the signal for As in the studied concentration range. The presence of a concentration of 10 $\mu g\,mL^{-1}$ of Se(IV) caused an increase of the signal for As, while a further increase of the concentration of the interferent to up to 500 $\mu g\,mL^{-1}$ again caused a decrease of the signal for As.

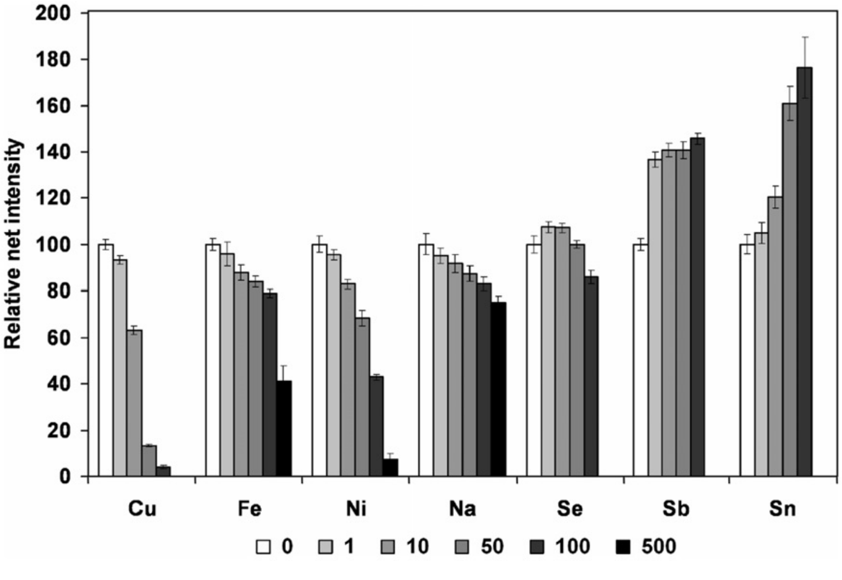

Figure 4. Influence of the concentrations of Cu(II), Fe(III), Ni(II), Na, Sb(III), Se(IV) and Sn(II) on the determination of As by ECHG-MPT-OES (5 replicate measurements).

Finally, the presence of the alkali metal Na was found to influence the As signal much less. At a concentration of 500 µg mL^{-1} of Na a reduction of the signal to 75% of its value in the absence of Na was observed. It is shown that the interferences in the case of a Pt electrode are not significantly different than for a carbon electrode [7].

3.5 *Use of masking reagents*

In order to reduce the interferences due to Cu(II), Ni(II) and Fe(III) in the generation and release of volatile hydrides of As in ECHG, the addition of the masking reagents L-cysteine or KI/ascorbic acid to the solutions was investigated. Solutions containing 50 or 100 µg mL^{-1} of one of the interferents mentioned before and 3 µg mL^{-1} of As were used.

As shown by the results in Figure 5, Cu(II) was found to cause the most severe interferences when determining As with ECHG-MPT-OES. In the presence of 100 µg mL^{-1} of Cu(II) the response for As was reduced to 4% of its value without Cu(II). By the addition of KI/ascorbic acid the signal for As was merely reduced to 74% of its value without Cu(II). The reduction of the interference of Cu(II) by the addition of KI/ascorbic acid could be explained by a precipitation of CuI. The presence of L-cysteine was also found to diminish the interferences from Cu(II), but here it was found to be less efficient.

Both masking reagents were also found to be useful for reducing the interference by Ni(II). In the case of 100 µg mL^{-1} of Ni(II) the signal for As decreased to 43% of its value without Ni(II) in the absence of masking reagents. In the presence of KI/ascorbic acid and L-cysteine, however, the signals for As, respectively, are still 94% and 99% of the signal obtained when Ni(II) is absent.

Finally, L-cysteine was also found to be a suitable masking reagent for Fe(III). For a solution containing 100 µg mL^{-1} of Fe(III) and 2% L-cysteine the signal for As was only reduced to 95% of the signal in the absence of Fe(III). When using KI/ascorbic acid as

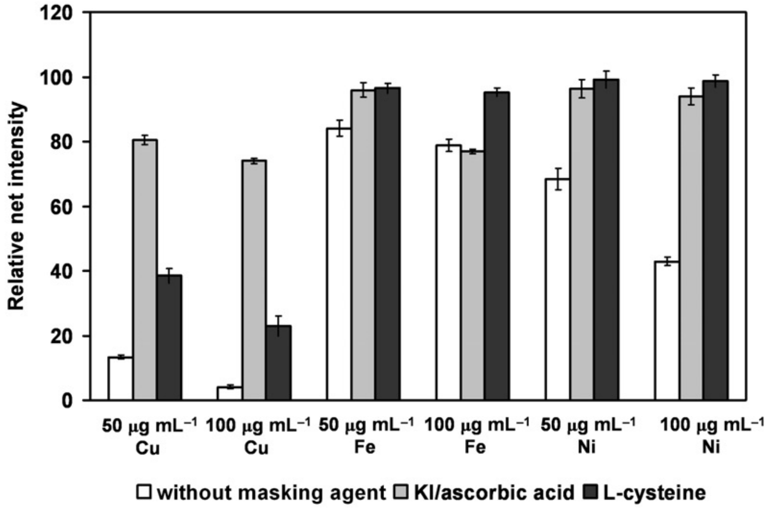

Figure 5. Influence of the addition of 2% of the masking reagents L-cysteine or KI/ascorbic acid (1 : 1) on the interferences caused by Cu(II), Fe(III) and Ni(II) in the determination of As by ECHG-MPT-OES (5 replicate measurements).

masking reagents the interferences caused by $50\,\mu g\,mL^{-1}$ of Fe(III) were reduced, whereas in the case of $100\,\mu g\,mL^{-1}$ of Fe(III) no decrease of the interferences could be observed.

From measurements with an As(III) solution of $3\,\mu g\,L^{-1}$ containing L-cysteine (2%) and one without L-cysteine it can be estimated that the depression of the signal was below 7%. Accordingly, the suppression of heavy metal interferences in the determination of As(III) by ECHG-MPT-OES through the addition of 2% L-cysteine to the analyte solutions is obvious.

3.6 *Analysis of real samples*

The accuracy obtainable with the procedure was investigated by analysing the certified coal fly ash reference sample (NIST SRM 1633a, Gaithersburg, USA) after sample digestion. The concentration of As found ($131 \pm 15\,\mu g\,g^{-1}$) well agreed with the certified data ($145 \pm 15\,\mu g\,g^{-1}$).

The developed ECHG-MPT-OES procedure could also be effectively used for the determination of As in two process waters from a copper refinery. In the refinery process of electrolyte copper, hydride forming elements and especially As can be found in the process waters and in the electrolytic slimes. Because of the high toxicity of As to man and environment, the legislation of the Federal Republic of Germany limits the amount of As in wastewaters from the production of non-ferrous metals to $0.1\,mg\,L^{-1}$ of As [20]. Moreover, elevated concentrations of As in the electrolysis bath solutions may influence the electrolysis itself. The concentration of As in process waters can be reduced by several different procedures [21] and, therefore, analytical methods allowing a strict monitoring of the concentration of As are required. The analysis results of ECHG-MPT-OES for the process waters of a copper refinery were found to agree well with those of FAAS and ICP-OES analysis using synthetic standards and standard addition as shown by the results in Table 3. The good agreement is understandable as after a dilution (of 1 : 400 for process water I and 1 : 5 for process water II) the interferent concentrations are below the critical values in the case of a complexation with L-cysteine (compare data in Table 3 and in Figure 5).

Table 3. Concentrations of As and the interferents in process water samples of a copper refinery.

	Concentration ($\mu g\,mL^{-1}$)					
	Process water I			Process water II		
	ECHG-MPT-OES	F-AAS	ICP-OES	ECHG-MPT-OES	F-AAS	ICP-OES
As	1630 ± 70	1590 ± 10	1620 ± 15	21.4 ± 0.8	20.9 ± 0.2	21.7 ± 0.3
Cu		84.6 ± 0.4			0.40 ± 0.01	
Ni		0.54 ± 0.01			<0.08*	
Fe		20.5 ± 0.1			4.93 ± 0.01	
Na		2190 ± 4			1190 ± 1	
Sb		1.9 ± 0.1			<0.3*	
Se		2.3 ± 0.1			<0.3*	
Sn		4.9 ± 0.2			<0.3*	

Note: *Below limit of detection.

However, it must be mentioned that ECHG-MPT-OES as used in this work from its instrumentation and consumables (gases and power) certainly is much less expensive than ICP-OES. In contrast to FAAS, however, ECHG-MPT-OES could be easily optimised for the simultaneous determination of several volatile hydride forming elements when asked for and this without any modifications of the instrumentation required.

4. Conclusions

It could be shown that ECHG-MPT-OES is well suitable for the determination of As in real samples such as the process water from a copper refinery after a thorough optimisation of the working parameters. It could also be shown that Cu(II), Fe(III) and Ni(II) cause a depression of the signal for As and Cu(II) was found to be the strongest interferent, while the hydride forming elements Sb(III) and Sn(II) increase the response for As. In this study it was found that by the addition of L-cysteine and KI/ascorbic acid interferences caused by the transition metals Cu(II), Fe(III) and Ni(II) in the case of a determination of As by means of ECHG-MPT-OES could be considerably reduced.

In future studies the use of masking reagents in the determination of other hydride forming elements and the use of three dimensional electrolysis cells with different cathode materials in the case of a detection of the signals by MPT-OES could be investigated.

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References

[1] H. Chen, I.D. Brindle, and X.C. Le, Anal. Chem. **64**, 667 (1992).
[2] A. Risnes and W. Lund, J. Anal. At. Spectrom. **11**, 943 (1996).
[3] P. Pohl, Trends in Anal. Chem. **23**, 87 (2004).
[4] H. Uggerud and W. Lund, J. Anal. At. Spectrom. **10**, 405 (1995).
[5] I. Rojas, M. Murillo, N. Carrion, and J. Chirinos, Anal. Bioanal. Chem. **376**, 110 (2003).
[6] C. Schickling, J. Yang, and J.A.C. Broekaert, J. Anal. At. Spectrom. **11**, 739 (1996).
[7] B. Özmen, F.-M. Matysik, N.H. Bings, and J.A.C. Broekaert, Spectrochim. Acta Part B **59**, 941 (2004).
[8] F. Laborda, E. Bolea, and J.R. Castillo, Anal. Bioanal. Chem. **388**, 743 (2007).
[9] S. Schermer, L. Jurica, J. Paumard, E. Beinrohr, F.M. Matysik, and J.A.C. Broekaert, Fresenius J. Anal. Chem. **371**, 740 (2001).
[10] B.W. Pack, G.M. Hieftje, Q. Jin, and Y.H. Shi, Anal. Chim. Acta **383**, 231 (1999).
[11] Q. Jin, G. Yang, A. Yu, J. Liu, H. Zhang, and Y. Ben, Pittcon'85, New Orleans USA, Abstract, 1171 (1985).
[12] Q. Jin, C. Zhu, M.W. Borer, and G.M. Hieftje, Spectrochim. Acta Part B **46**, 417 (1991).
[13] Y. Lin, X. Wang, D. Yuan, P. Yang, B. Huang, and Z. Zhuang, J. Anal. At. Spectrom. **7**, 287 (1992).
[14] N.H. Bings, Z. Stefanka, and S. Rodriguez Mallada, Anal. Chim. Acta **479**, 203 (2003).
[15] W.-W. Ding and R.E. Sturgeon, J. Anal. At. Spectrom. **11**, 421 (1996).

[16] L. Tomlinson, J. Electrochem. Soc. **111**, 348 (1964).

[17] H.W. Salzberg and B. Goldschmidt, J. Electrochem. Soc. **107**, 348 (1960).

[18] F. Laborda, E. Bolea, and J.R. Castello, J. Anal. At. Spectrom. **17**, 727 (2002).

[19] E. Denkhaus, F. Beck, P. Bueschler, R. Gerhard, and A. Golloch, Fresenius J. Anal. Chem. **370**, 735 (2001).

[20] Bundesministerium für Umwelt Naturschutz und Reaktorsicherheit, *Abwasserverordung*, BGBl. Teil I, 1108 (2004).

[21] A.J. Monhemius and P.M. Swash, JOM **51**, 30 (1999).