Talanta 100 (2012) 45–50

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Analytical performance of a lab-made concomitant metal analyzer to generate volatile species of Ag, Au, Cd, Cu, Ni, Sn and Zn using 8-hydroxyquinoline as a reaction media

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ARTICLE INFO

Article history:
Received 20 April 2012
Received in revised form
22 July 2012
Accepted 27 July 2012
Available online 16 August 2012

Keywords:
Concomitant metal analyzer
Chemical vapor generation
Multi-element detection
8-hydroxyquinoline

ABSTRACT

This study evaluated the main parameters affecting Ag, Au, Cd, Cu, Ni, Sn and Zn vapor generation using a lab-made concomitant metal analyzer (CMA) as a reaction chamber and gas–liquid separator. The modifier used in the reaction media was 8-hydroxyquinoline, and Inductively-Coupled Plasma Optical Emission Spectrometry was used as detection technique. The performance of the lab-made concomitant analyzer was compared with the performance of a continuous flow gas–liquid separator and of a cyclonic spray chamber. Standards were prepared in acid media and included 1 mg L^{-1} of Co as a catalyzer. The optimum concentrations of the reagents in the standards were: 450 mg L^{-1} of 8-hydroxyquinoline and 0.4 M nitric acid. The optimum concentration of sodium borohydride to generate the vapors was 2.25% (w/v) (prepared in 0.4% (w/v) NaOH). The volatile species were swept from the CMA to the torch by an argon flow of 0.6 mL min^{-1}. The use of the CMA led to an improvement of the detection limits for some elements compared to conventional nebulization: 1.1 μg L^{-1} for Ag, 7.0 μg L^{-1} for Au and 4.3 μg L^{-1} for Sn. The limit of detection for Cu was 1.4 μg L^{-1} and for Ni 22.5 μg L^{-1}. The direct mixing of the reagents on the spray chamber was not effective for Cd and Zn; a deviation of the linearity was observed for these elements.

1. Introduction

The efficiency of the generation of volatile species depends on chemical and instrumental parameters. Variables associated with the generation of the volatile species and its separation and transport to the detection unit have to be studied [1] for each chemical vapor generator. An efficient separation/transport is vital to avoid losses, because the volatile species may be unstable or may be deposited on the surfaces in contact (specially if the species are nanoparticles) [2,3].

Several devices have been developed for chemical vapor generation of noble and transition metals. Some of them use spray chambers (Scott double pass or cyclonic) as gas–liquid separators, and the volatile species are transported directly to the detection unit [4–11]. Other devices include: frit based gas–liquid separators [12], U tube gas–liquid separators and hydrostatic gas–liquid separators [2, 13–15]. In recent years, a gas–liquid separator including thin film technology [16], and a heated quartz multiatomizer with a heated inlet arm at 300 °C [3] have also been developed.

The Concomitant Metal Analyzer was developed by Pohl et al. [6,7,10,11]. It is a generation/separation system consisting of a cyclonic spray chamber and a concentric nebulizer that has been modified with several inlets at the bottom. The sample and reductant are introduced into two separate tubes in the bottom of the spray chamber where the reaction takes place. The volatile species and the excess of hydrogen generated are swept to the plasma torch by a flow of carrier Ar introduced by the Ar nebulizer inlet (the sample inlet of the nebulizer was usually blocked). These authors [10] optimized the conditions for the generation of volatile species of Au, Pd and Pt using HG-ICPOES and the Concomitant Metal Analyzer. In a subsequent paper the same authors studied the analytical performance of the method, obtaining excellent results [11]. The detection limits obtained were better than those obtained using pneumatic nebulization. They also evaluated the behavior of the system for Os, Rh and Ru using VG ICP-OES [7]; detection limits were an order of magnitude lower than those obtained introducing the samples by pneumatic nebulization. A similar system was used by Matusiewicz et al. [17] to determine Ag, Au, Pt, Pd and Rh by MIP-OES. These authors inserted on an ultrasonic nebulizer three inlets to introduce the sample, the reductant and the acidified solution. The ultrasonic nebulizer was coupled to the cyclonic chamber, and it might help to release the species to the gaseous phase (e.g. by

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http://dx.doi.org/10.1016/j.talanta.2012.07.072

dispersing the nanoparticles). This is the reason why they obtained better results for Pt, Pd and Rh than Pohl et al. [7,11].

Another strategy to improve the efficiency of chemical vapor generation of noble and transition elements is to control the reaction media. Organic acids [16,18], buffers [19], control of temperature [20] and different modifiers [16,18,21–23] have been used so far to increase the reaction yield. Thus, 8-hydroxyquinoline has been used for simultaneous determination of noble and transition metals [24–26], o-phenanthroline for Cu determination, DDTC for the determination of Au [19] and Cu [18], surfactants such as Triton X-100 [2,14,15] and CTAB [23] for the determination of Ag and Zn, and ionic liquids for the determination of Cu, Au, Ag [27] and Ni [22].

This work describes the analytical performance of a lab-made concomitant metal analyzer for the simultaneous generation of noble and transition metallic volatile species (Ag, Au, Cd, Cu, Ni, Sn and Zn) using 8-hydroxyquinoline as a reaction media modifier. The performance of this system was compared with the use of a continuous flow forced outlet gas–liquid separator and a 100 μL reaction loop.

2. Experimental

2.1. Instrumentation

An Optima 3300 DV^{TM} ICP-OES spectrometer (Perkin Elmer, Norwalk, USA) was used to perform all the experiments.

A lab-made spray chambers (Fig. 1) based on the Concomitant Metal Analyzer system was used in combination with a Gem Cone^{TM} nebulizer (Perkin Elmer, Norwalk, USA) in the vapor generation mode. The spray chamber was made in the *Unidade de Soprado de Vidro e Cuarzo Científico* (University of Santiago de Compostela). The performance of the spray chamber was compared with conventional sample introduction using a cyclonic chamber and the Gem Cone^{TM} nebulizer, and with a vapor generation system consisting of a 100 μL reaction loop and a lab-made forced outlet gas–liquid separator connected to the torch base using a 60 cm PTFE tube and a small Tygon tube. All the connections were made with PTFE tubing of 0.5 mm id.

A Minipuls 3 Peristaltic Pump (Gilson, Villiers-le-Bel, France) was used to pump the liquid waste from the spray chambers or the forced outlet gas–liquid separator.

For comparison purposes, sample flow rates employed on the three systems were the same 1.5 mL min^{-1}, even though better results can be obtained on the forced outlet system using higher flow rates [24].

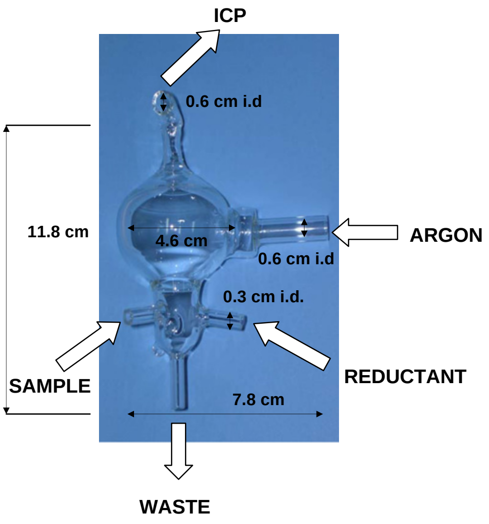

Fig.1. Lab-made CMA spray chamber.

Table 1
Operating parameters for ICP-OES.

λ_{Ag}/nm	328.068
λ_{Au}/nm	242.795
λ_{Cd}/nm	214.440
λ_{Cu}/nm	324.762
λ_{Ni}/nm	231.604
λ_{Sn}/nm	189.927
λ_{Zn}/nm	213.857
Power of plasma generator/W	1350
Outer Ar flow rate /L min^{-1}	15
Purge Ar flow rate /L min^{-1}	0.6 (lab-made CMA) 0.75(forced outlet GLS) 0.8 (cyclonic spray chamber)
Intermediate Ar flow rate /L min^{-1}	0.5
Viewing height/mm	15 Axial mode
Purge gas flow	Normal
Read delay/s	40
Replicates	4
Integration time/s	5

2.2. Reagents and solutions

Stock solutions of 1000 mg L^{-1} were purchased from BDH, Poole, UK (Co, Ni, Ag, Sn); Fluka, Steimheim, Switzerland (Au); Merk, Darmstad, Germany (Cd, Cu, Zn); 8-hydroxyquinoline was from Fluka (Steinheim, Switzerland).

Nitric acid 69% (w/v) (Hiperpur) and hydrochloric acid 35% (w/v) (Hiperpur) from Panreac SA (Barcelona, Spain) were used to generate the vapors. $NaBH_4$ (Avocado Research Chemicals Ltd., Heysham, UK) was also used for vapor generation. Ultrapure water (specific resistance of 18 MΩ cm) was obtained from a Milli-Q purification system (Millipore Corporation, Massachussets, USA). All the glassware and materials were cleaned using ultrapure water, soaked in nitric acid for 48 h and rinsed again with ultrapure water at least three times. Afterwards, material was stored dry and covered.

2.3. Procedures

2.3.1. Standards preparation

Different concentrations of the elements were added to solutions containing 1 mg L^{-1} of Co and 450 mg L^{-1} of 8-hydroxyquinoline. The optimum concentration of nitric acid was 0.4 M. For comparison purposes the results obtained with the lab-made CMA were compared with those obtained using a forced outlet gas–liquid separator. The procedure to perform those measurements was previously described [24].

2.3.2. Determination using VG-ICP-OES

Vapor generation from noble and transition metal acidified solutions was performed after mixing acidified standards with sodium borohydride. Reagents were mixed inside the bottom of the CMA chamber. The Ar flow employed was 0.6 L min^{-1}. Vapor generation and detection conditions using ICP-OES are summarized in Table 1.

3. Results and discussion

3.1. Preliminary experiments

Different parameters affecting volatile species generation (sample flow, reductant flow and waste flow) were selected before the systematic optimization of the vapor generation conditions. Two criteria were used to choose the best combination of flow rates: 1) sample and reductant flow rates should be equal; 2) the plasma should be completely stable. A blank and a standard solution containing 1 mg L^{-1} of each metal, 225 mg L^{-1} of 8-hydroxyquinoline and 0.45 M nitric acid, were used for the preliminary experiments. Cobalt at a fixed concentration of 1 mg L^{-1} was included in all the standards as in previous studies [21,24–26], because it acts a catalyst for vapor generation, for example in the case of Cd [26]. The reductant concentration was 1.75% (w/v) and the Ar flow was 0.75 L min^{-1}. Intensities of emission for the analytical lines were measured in triplicate for each solution. Under these conditions the best results were obtained using sample and reductant flow rates of 1.5 L $min^{-1}$and a waste flow rate of 7.7 L min^{-1}. We tried to introduce an additional sample flow through the Gem Cone^{TM} nebulizer, but it was not possible without extinguishing the plasma.

Then, we optimized the following parameters: Ar flow, nitric acid concentration and 8-hydroxyquinoline concentration and reductant concentration.

3.2. *Optimization of operational variables*

A univariate approach was carried out to obtain the optimum values of the main operational parameters. Standards containing 0.45 mg L^{-1} of each element (except for Sn: 0.15 mg L^{-1}) were prepared for all the following experiments, together with the reagents blanks. Intensities of emission for the analytical lines were measured in triplicate for each standard solution, and afterwards a subtraction of the intensity of the corresponding blank was performed.

3.2.1. *Optimization of argon flow rate*

The influence of argon flow (0.6, 0.8, 1.0 mL min^{-1}) was evaluated, and results are shown in Fig. 2(a). A compromise argon flow value (0.6 mL min^{-1}) was selected. This argon flow was optimum for the detection of all elements.

3.2.2. *Optimization of acid concentration*

Acid concentration in the standards containing 225 mg L^{-1} of 8-hydroxyquinoline was optimized using 1.17% (w/v) sodium borohydride. Concentrations ranging from 0.25 to 0.55 M of nitric acid were evaluated. Normalized intensities for nitric acid are shown in Fig. 2(b). It can be observed that optimum concentration of nitric acid was 0.4 for all the elements. The same value obtained by Peña-Vázquez et al. in previous work [24]. According to this result and experiments using other modifiers performed in our laboratory, the optimum acidity might be dependent not only on the different elements but also on the modifier employed. Thus, several modifiers were tested (o-phenanthroline, diethyldithiocarbamate, CTAB, CTAB + the ionic liquid 1-butyl-3-methylimidazolium bromide) in a forced outlet gas–liquid separator, and the optimum concentration of nitric acid ranged from 0.3 M (CTAB + ionic liquid) to 0.6 M (CTAB) (unpublished results).

3.2.3. *Optimization of 8-hydroxyquinoline concentration*

Different concentrations of 8-hydroxyquinoline (25 mg L^{-1}, 150 mg L^{-1}, 300 mg L^{-1}, 450 mg L^{-1}, 600 mg L^{-1}, 750 mg L^{-1} and 900 mg L^{-1}) were tested to generate the volatile species. Standards were prepared in 0.4 M nitric acid and the corresponding volume of 8-hydroxyquinoline was added (from a solution containing 3 g L^{-1} of 8-hydroxyquinoline and 0.3 M hydrochloric acid). A solution of 1.75% (w/v) of sodium borohydride was used as reductant agent.

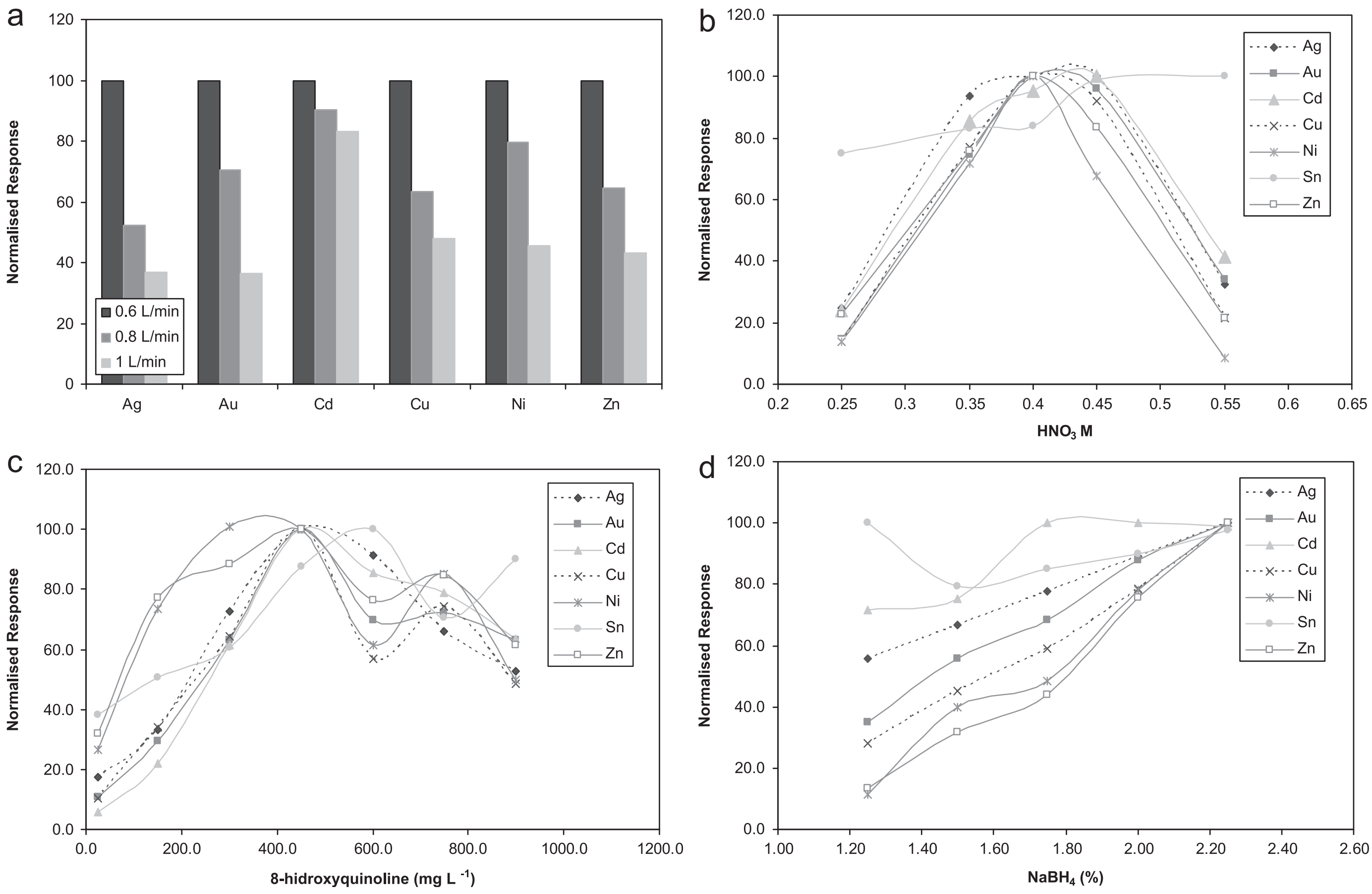

Fig.2. Optimization of operating conditions for the lab-made modified CMA: (a) Ar flow (b) Nitric acid (c) 8-hydroxyquinoline and (d) Sodium borohydride,

Optimization of 8-hydroxyquinoline concentration is shown in Fig. 2(c). It can be observed that the optimum concentration of 8-hydroxyquinoline was 450 mg L^{-1} for all the elements except for Sn. There is a local minimum for most elements at 600 mg L^{-1} that coincide with the maximum signal for Sn. These phenomena were also observed in other experiments of this work (see also Fig. 2(b) and (d)); it could be deduced that the mechanism for the formation of the volatile species is different for Sn. The optimum amount of 8-hydroxyquinoline for the lab-made CMA is 10 times higher than the optimum value employed using the forced outlet gas–liquid separator system. Previous studies showed that the use of higher amounts of 8-hydroxyquinoline (250 mg L^{-1}) to determine metals in steels [25] (high metallic contain samples), or the use of higher flow rates [26] were necessary. In this case the volatile species were generated in a recipient that was three times larger and without a reaction loop, allowing the reagents to mix for a longer period of time. The high concentration of 8-hydroxyquinoline is also suitable as previously shown to avoid inter-element interferences in high metal content samples [25].

3.2.4. *Optimization of reductant concentration*

Variation in the corrected intensities was studied when using different concentrations of $NaBH_4$ (1.25% (w/v), 1.5% (w/v), 1.75% (w/v). 2% (w/v), 2.25% (w/v)). The reductant was stabilized with 0.5% (w/v) NaOH. Blank corrected signals were normalized for comparison purposes; a value of 100 corresponded to the highest intensity obtained for each element. Normalized corrected intensities for the different elements are shown in Fig. 2(d). It can be observed that the optimum concentration of sodium borohydride was 2.24% (w/v) for all the elements.

3.2.5. *Optimized measurement conditions*

As a conclusion, the optimum values of the parameters influencing simultaneous vapor generation of Ag, Au, Cd, Cu, Ni, Sn and Zn were the following: argon flow=0.6 L min^{-1}, $[HNO_3]$=0.45 M, $[NaBH_4]$: 2.25% (w/v), [8-hydroxyquinoline]=450 mg L^{-1}, sample flow/reductant flow ratio: 1:1, sample flow and reductant flow 1.5 mL min^{-1} respectively, and waste flow 7.7 mL min^{-1}. A solution containing 0.1 M HCl was introduced between measurements to avoid sensitivity drifts.

3.3. *Analytical performance of the system*

3.3.1. *Calibration curves*

Calibration standards were prepared using standards that contained the following element concentrations: 0, 0.075, 0.15, 0.30 and 0.45 mg L^{-1} of Ag, Au, Cd, Cu, Ni, and Zn (concentrations for Sn were lower: 0, 0.025, 0.05, 0.1, 0.15 mg L^{-1}). All the standards had a concentration of 1 mg L^{-1} of Co, 0.4 M of nitric acid and 450 mg L^{-1} of 8-hydroxyquinoline. The linearity of the calibration graphs was good for all the elements ($r < 0.995$). Table 2 includes calibration graphs that were obtained using the vapor generation with the lab-made CMA, or a lab-made forced outlet GLS, and conventional nebulization (cyclonic spray chamber and Gem Cone nebulizer, both from Perkin Elmer). The sensitivity increased for Ag, Au, Cu and Sn: 3.1, 4.8, 1.1 and 14 times respectively. As expected, the sensitivity increased for Au from 2.4 times [11] to 4.8 times when using 8-hydroxyquinoline as a modifier. The analytical performance improved providing a linear calibration curve (r from 0.9863 [11] to 0.999).

In the case of Cd, data cannot be modeled by a first order linear regression. A better option would be to fit the data to a curve using a polynomial regression function. A similar calibration curve was previously employed to determine Ag by Musil et al. [3] when they increased the reaction transport for Ag to its maximum using a heated tube as transfer line. The behavior of Ni and Zn was very similar. We experienced a loss of sensitivity by using the concomitant metal analyzer in the present work in comparison with the sensitivity obtained using the forced outlet gas–liquid separator. The slope of the calibration graph decreased a percentage of 39.4% for Ni and 60.2% for Zn. It seems that a longer controlled reaction time over the surface of a smaller gas–liquid separator [12] or the introduction of a reaction loop [20,28,29] would be needed to improve the characteristics of these introduction system.

Table 2
Analytical performance for detection using ICP-OES.

	Neb.	Forced outlet GLS	CMA	Neb.	Forced outlet GLS	CMA
	Ag (328.062 nm)			**Au (242.795 nm)**		
Slope	36090.0	Non linear	**112,345.2**	3333.9	5088.0	**15968.1**
R	1.0		**0.996**	0.995	0.997	**0.999**
LOD (μg/L)	2.7		**1.1**	12	8.1	**7.0**
LOQ (μg/L)	9.1		**3.9**	41.0	27.0	**22.9**
RSD (%)	5.4		**9.4**	2.4	2.9	**10.8**
	Cd (214.440 nm)			**Cu (324.752 nm)**		
Slope	14,088.0	13,751.0	Non linear	94,114.0	35,005.0	101,567
R	1.0	0.998		1.000	0.997	0.999
LOD(μg/L)	0.8	3.3		1.1	4.7	1.4
LOQ(μg/L)	2.7	10.9		3.6	15.5	4.8
RSD (%)	0.8	8.5		2.0	3.1	10.8
	Ni (231.604 nm)			**Sn (189.927 nm)**		
Slope	7315.3	1768.2	1072.3	264.1	5310.9	3840.1
R	1.0	0.994	0.999	0.996	0.994	0.999
LOD(μg/L)	2.6	8.4	22.5	28.2	1.6	4.3
LOQ(μg/L)	8.8	27.9	75.1	94.2	5.4	14.3
RSD (%)	1.8	4.1	9.2	40.6	5.4	3.5
	Zn (213.857 nm)					
Slope	8175.7	5203.1	2071.2			
R	1.0	0.992	0.999			
LOD(μg/L)	1.4	5.5	14.4			
LOQ(μg/L)	4.5	18.3	48.1			
RSD (%)	0.9	5.8	6.3			

3.3.2. *Limits of detection*

The limits of detection were calculated after analyzing 11 times a reagent blank using the method developed. The limit of detection (LOD) corresponds to the element concentration that is three times the standard deviation of the measurement of the blanks. Similarly, the limit of quantification (LOQ) is the element concentration corresponding to 10 times the standard deviation of the blank. Calculated values for the selected analytical lines are shown in Table 2, together with the values obtained using conventional nebulization and a chemical vapor generation system with a forced outlet gas–liquid separator. The system provided good results in the case of Ag, Au and Sn. We must point out the low detection limit obtained for Ag using of this procedure. Limits of detection for this element have decreased over the last 10 years. Different methods have been developed, with limits of detection ranging from $mg\,L^{-1}$ to $\mu g\,L^{-1}$. Limits of detection of $3300\,\mu g\,L^{-1}$ were reported [30] in early studies using CVG-AAS with a quartz atomizer, $15\,\mu g\,L^{-1}$ using the multiatomizer [14], and $15\,\mu g\,L^{-1}$ using CVG-AFS [27] and an ionic liquid as a reaction modifier. In previous studies using 8-hydroxyquinoline, lower LODs were obtained for Ag ($50\,\mu g\,L^{-1}$ using a multielement CVG-ICPOES method) [24]; in another study using CVG-HRCSAAS for monoelement determination the LOD was $14\,\mu g\,L^{-1}$ [26]. In the present paper, the limit of detection obtained is in the same order of magnitude as the best limits of detection for Ag in the literature. Musil et al. [3] obtained a LOD of $1.1\,\mu g\,L^{-1}$ on the multiatomizer by heating the transfer line to avoid transport losses, and Duan et al. [12] obtained a LOD of $0.6\,\mu g\,L^{-1}$ using the ICPOES. It is important to stress how simple the procedure is. It does not use heating devices [3] or phosphoric acid or complex gas–liquid separators [12]. This is what makes the method appealing for further research. Pohl et al. [34] used a commercial CMA dual-sample introduction system with a concentric Meinhard nebulizer and obtained better limits of detection for Sn ($2.1\,\mu g\,L^{-1}$), Ni ($4.9\,\mu g\,L^{-1}$) and Zn ($2.0\,\mu g\,L^{-1}$). However, the limit of detection for Cu ($1.2\,\mu g\,L^{-1}$) is similar to that obtained in the present study working only in the vapor generation mode. It would be interesting to couple a nebulizer to our spray chamber and reoptimise the system in dual mode taking into account the special conditions for the generation of vapors from metal solutions.

4. Precision

Precision was estimated after performing 11 measurements of one standard containing $0.15\,mg\,L^{-1}$ of each metal, except for Sn ($0.05\,mg\,L^{-1}$). Average intensities, standard deviations and relative standard deviations (RSDs) were calculated. Obtained RSD values for the selected lines for the different elements are listed in Table 2. It seems that the closer the reaction occurs to the ICP torch, the greater the deviations on the measurements and the higher the RSDs. The RSDs obtained in this work are acceptable, around 10% or lower for all elements. The difference between the RSD obtained for Sn (3.5%) and the RSDs obtained for the other elements (range: 9–11%) might be the result of differences on the reaction mechanisms and reaction products. Furthermore, it is clear from the difference on the RSDs obtained using a forced outlet gas–liquid separator and a transfer line (range: 3.5–5.8 for Au, Cu, Ni, Sn and Zn) that there might be problems due to the interface between the ICP and the chemical vapor generation reaction system. These problems were mentioned by Matousek et al. [14] on an early work. The sample introduction method influences parameters of the ICP such as electron density, excitation temperature, etc. These parameters affect the analytical performance of the equipment. Recently, the spectroscopic characteristics of the ICP when it is combined with hydride generation [31,32] or a dual mode sample introduction [33,34] have been studied. The authors [31–34] pointed out that reductant concentration determines the amount of hydrogen generated and has a positive effect on the atomization. Pohl et al. [34] mentioned the scarce literature existing on the topic. When performing vapor generation of noble and transition metals it is necessary to avoid transport losses. Two strategies have been used to do so: short/heated transfer lines [20,28,29] and spray chambers as gas–liquid separators [5–11,35]. Both approaches provided interesting results; in most cases the improvements on sensitivity where high in comparison with the limits of detection obtained. Possibly, the study of the relationship between $Ar/H_2O/H_2$ going to the ICP in this kind of systems could improve the ICP stability, and consequently improve precision and the detection limits.

5. Conclusions

Variables influencing Ag, Au, Cd, Cu, Ni, Sn and Zn simultaneous determination by VG-ICP-OES have been optimized in the present work. The direct mixture of reagents in the bottom of a spray chamber using 8-hydroxyquinoline as a chemical modifier turned out to be a sensitive procedure for the generation of volatile species of Ag, and Au, and also useful for the generation of tin hydride. The simplicity of this approach makes it interesting for further research; studies of the interface between the reaction and the ICP should be developed in the future.

Acknowledgments

J. Villanueva-Alonso acknowledges the financial support of the Government of Spain for her FPU scholarship. This work is part of a project sponsored by the Xunta de Galicia, Ref. PGIDIT07 PXIB209034PR.

The authors acknowledge the competence and careful work of members of the *Unidade de Soprado de Vidro e Cuarzo Científico* of the University of Santiago de Compostela.

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