Influence of Surfactant and Ionic Liquid Media on Vapor Generation and Determination of Ag, Au, Cd, Cu, Ni, Sn, and Zn Using ICP-OES

Julia Villanueva-Alonso, Ana Suárez-García, Elena Peña-Vázquez, and Pilar Bermejo-Barrera

Department of Analytical Chemistry, Nutrition and Bromatology, Faculty of Chemistry, University of Santiago de Compostela, Avenida de las Ciencias s/n, E-15782, Santiago de Compostela, Spain

ABSTRACT

In this study, the main parameters affecting Ag, Au, Cd, Cu, Ni, Sn, and Zn vapor generation in a surfactant reaction media of cetyl trimethyl ammonium bromide (CTAB) were evaluated. Detection using inductively coupled plasma optical emission spectrometry has been optimized. Improvements in the analytical performance for Ag and Ni were also obtained when CTAB was combined with the ionic liquid 1-butyl-3-methylimidazolium. Standards (1 mg L^{-1}) were prepared in acid media. The optimum concentrations of the reagents in the standards were: $2.5 \times 10^{-5} \text{ M}$ (CTAB) and 0.6 M (nitric acid), when only CTAB was used. When both modifiers were combined, the concentrations were: $2.5 \times 10^{-3} \text{ M}$ of 1-butyl-3-methylimidazolium bromide and $1.5 \times 10^{-5} \text{ M}$ CTAB. In this case, 0.3 M of nitric acid was added. The optimum concentration of sodium borohydride to generate the vapors was

$2.2\% \text{ (w/v)}$ in $0.05\% \text{ (w/v)}$ NaOH. These vapors were swept from the forced outlet of a lab-made gas-liquid separator to the torch with an argon flow of 0.7 mL min^{-1} .

The limits of detection ranged from $0.4 \text{ } \mu\text{g L}^{-1}$ Cu to $6.9 \text{ } \mu\text{g L}^{-1}$ Au. The detection limit for silver improved three-fold when CTAB was used together with 1-butyl-3-methylimidazolium bromide (from 14.3 to $4.9 \text{ } \mu\text{g L}^{-1}$). Relative standard deviations were below 5% ($n=11$) for all of the elements, except for Cd ($11.3 \text{ } \mu\text{g L}^{-1}$).

Since best results were obtained for most elements using only CTAB, a study of interferences for this modifier was performed. It was observed that a surfactant agent, such as CTAB, was a better reagent to avoid interferences than a complexing agent, such as 8-hydroxyquinoline. Moreover, the method showed good accuracy when determining Cd, Cu, Ni, and Zn in a wastewater reference material.

(e.g., As, Se, or Pb) (12). Micelles (most of them consisting of an aggregation of ionic amphiphile monomers with the hydrophobic or the hydrophilic portions of the surfactant molecule associated to exclude water or the non-polar solvent, respectively) and vesicles (closed bilayer aggregates) trap the analyte in a controlled environment. Surfactants can enhance the efficiency in the transport of volatile species, improve the reaction kinetics, stabilize some unstable species, and produce changes in the selectivity of the reactions (13).

Matousek et al. (14) suggested that nanoparticles were generated with borohydride in the case of noble and transition element solutions. These particles would become more hydrophobic when interacting with the surfactant, and could be extracted from the solutions together with the nascent hydrogen. Feng et al. (15) proposed that the surfactants could reduce surface tension and promote the release of the volatile species.

Fernández de la Campa et al. (16) studied how surfactant-based organized assemblies affected hydride generation of vapors of As, Pb, Cd, Hg, Se, and Sn. They compared various types of surfactants that form vesicles or micelles such as CTAB: cationic surfactants (cetyl trimethylammonium bromide, DDAB: didecyltrimethylammonium bromide), anionic surfactants (SLS: sodium lauryl sulphate, DHDP: dihexadecylphosphate), non-ionic surfactants (Triton® X-100) and zwitterionic surfactants (ZW) (13,16). Cationic surfactants such as CTAB and DDAB produced increases in the signals of Sn, Hg, and Pb (16,17). In other studies,

INTRODUCTION

One of the most important factors affecting the generation of vapors obtained from transition and noble metal solutions is the composition of the reaction media. Different additives have been added to increase the yield in the production of vapors. Complexing agents such as 8-hydroxyquinoline (1-4), phenanthroline (1,5), diethyldithiocarbamate (DDTC) (6-8), thiourea

(9), EDTA, ascorbic acid, ferron and L-cysteine (1) have been tested. Metals such as Pd (6,10) and also Co (2-4) and Ni (1,5,9,11) have been included as catalyzers of the reaction.

Surfactants are the most useful option for generating an organized media when producing vapors for analytical purposes. Surfactants have been used to form vesicles, micelles, emulsions, or microemulsions to improve cold vapor analytical techniques (determination of Cd and Hg) and hydride generation of elements that typically form hydrides

*Corresponding author.

E-mail: pilar.bermejo@usc.es

Tel.: + 34 881814266

Fax: + 34 981 547141

the authors also compared the different surfactants for the generation of Cd vapors (18-20). Best results were obtained when using cationic vesicles of DDAB (limit of detection: $1 \mu\text{g L}^{-1}$) (18). In this case, simultaneous generation of the vesicles by sonication and vapor generation was performed.

Other authors have selected two types of surfactants to perform vapor generation with borohydride from noble and transition element solutions: Triton X-100 and CTAB. Triton X-100 was used to determine Ag (10,21) and was tested in the generation of vapors of Cu, Pd, Ag, Pt, Au, Co, Ni, Rh, Mn, Cd, and Sb when including different materials such as a Ryton® spray chamber or a glass spray chamber in the vapor generation system (15). The results were especially good for Rh. Triton X-100 is usually combined in the experiments with Antifoam B, a mixture of non-ionic surfactants. Triton X-100 and Antifoam B have been recently used together with DDTC to generate vapors of Au in a flow injection system coupled on-line with a quartz tube multi-atomizer for atomic absorption spectrometry (22).

Sun et al. (1,11) selected the cationic surfactant CTAB vs. SLS and SDBS (sodium dodecyl benzene sulfonate) to determine Zn using vapor generation and atomic fluorescence spectrometry (AFS) as a detection technique. CTAB was the compound that produced the highest increase in sensitivity (limit of detection of 1.6 ng L^{-1} vs. 3.9 ng L^{-1} in aqueous media) and the best precision (RSD aqueous media = 2.3% vs. RSD CTAB = 1.6%). Another important advantage of the use of CTAB was that it diminished interferences from Ag, As, Bi, Ca, Cr, Cu, Fe, Ge, Hg, Mg, Pb, Se, Sn, and Te.

Ionic liquids consist of the combination of organic cations and anions. The most common cations

are: 1-alkyl-3-methylimidazolium, N-alkylpyridinium, tetraalkylammonium, or tetraalkylfosfonium. The most common anions are: hexafluorophosphate, tetrafluoroborate, trifluoromethylsulfonate, bis-trifluoromethyl sulfonilamide, trifluoroethanoate, acetate, nitrate, and halides. Ionic liquids present some interesting properties such as low vapor pressure, good thermal stability, variable viscosity, and can be mixed with organic solvents and water (16).

In recent years, room temperature ionic liquids have also shown their potential for analytical applications in the determination of Au (23) and in the simultaneous determination of Ag, Au, and Cu (24). Moreover, one ionic liquid (1-butyl-3-methylimidazolium bromide) combined with DDTC showed a synergistic improvement in the chemical vapor generation of Ni (25). Ammonium pyrrolidinedithiocarbamate (APDC) has also been combined with room temperature ionic liquids to enhance vapor generation of Fe, Co, and Ni (26,27); Zn (28); Pb, Cd, and Bi (29).

Finally, surfactants are able to self-aggregate depending on their structure, concentration, and solubilization media. There are some examples in the literature on how this aggregation process can be modified in the presence of ionic liquids (30). Modaresi et al. (31) studied the aggregation of CTAB in the presence of ammonium-based ionic liquids in aqueous solution, concluding that this influence is due to the formation of mixed micelles. On the other hand, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was found to prevent CTAB aggregation by Fletcher et al. (32). The formation of microemulsions in the presence of an organic solvent (toluene, pentanol), CTAB, and the ionic liquid (IL) (1-ethyl-3-methylimidazolium-ethylsulfate or 1-ethyl-3-methylimidazolium-hexylsulfate)

has also been reported by Rabe et al. (33).

The objective of the present work was to select the optimum conditions for performing the simultaneous determination of noble and transition metals (Ag, Au, Cd, Cu, Ni, Sn, and Zn) by inductively coupled plasma optical emission spectrometry (ICP-OES) using CTAB as a modifier agent of the reaction media, and afterwards to test CTAB to avoid interferences. The combined performance of CTAB and 1-butyl-3-methylimidazolium bromide was also evaluated.

EXPERIMENTAL

Instrumentation

An Optima™ 3300 DV ICP-OES (PerkinElmer, Inc., Shelton, CT, USA) was used to perform all experiments. A glass gas-liquid separator with forced outlet was used (2). The separator was connected to the torch using a 60-cm PTFE tube, and the liquid was pumped to waste using a Minipuls™ 3 peristaltic pump (Gilson, Villiers-le-Bel, France). All connections in the vapor generation system were made of PTFE tubing of 0.5 mm i.d., including the 100- μL reaction loop. The Optima spectrometer system includes a three-channel, software-controlled peristaltic pump to introduce the sample solutions and the reductant.

A cyclonic chamber and a Gem-Cone™ nebulizer (PerkinElmer, Shelton, CT, USA) were also used to compare conventional nebulization with the performance of the vapor generation system.

Stock Solutions and Reagents

Stock solutions of 1000 mg L^{-1} were purchased from BDH, Poole, UK (Co, Ni, Ag, Sn); Fluka, Steinheim, Switzerland (Au); Merck, Darmstadt, Germany (Cd, Pb, Zn); and PerkinElmer, Shelton, CT, USA (Cu, Fe).

Solutions of 69% nitric acid (Hyperpur®) and 35% hydrochloric acid (Hyperpur®) from Panreac SA (Barcelona, Spain) were used to generate the vapors. NaBH₄ (Avo-cado Research Chemicals Ltd., Heysham, UK) was also used for vapor generation. CTAB was purchased from Sigma Chemicals (St. Louis, USA) and 1-butyl-3-methyl-imidazolium bromide from Fluka-Sigma Chemicals (St Louis, MO, USA). Other surfactants also tested in the present work included: sodium lauryl sulfate (SLS, from Merck, Darmstadt, Germany), sodium dodecylbenzene sulfonate (SDBS), Aerosol-OT, and Triton-X100 (Merck, Darmstadt, Germany), combined with antifoam B (Sigma Chemicals, St Louis, MO, USA).

Accuracy of the method was tested using a certified reference material for measurement of the elements in wastewaters (SPS-WW2 Batch 110) provided by Spectrapure Standards, Oslo, Norway.

Ultrapure water (specific resistance of 18 MΩ cm) was obtained from a Milli-Q® purification system (Millipore Corporation, USA). All glassware and materials were cleaned using ultrapure water, soaked in nitric acid for 48 hours, then rinsed again with ultrapure water at least three times. Afterwards, the material was stored dry and covered.

Procedures

Preparation of Standards

Different concentrations of the elements were added to solutions containing 1 mg L⁻¹ of Co (catalyst for vapor generation) (4) and 2.5×10⁻⁵ M of CTAB (concentration optimized in the present study). For all of the elements, except Ag, the highest sensitivity was provided when the standards were prepared in nitric acid instead of hydrochloric acid. The optimum concentration of nitric acid was 0.6 M.

Determination by VG-ICP-OES

Vapor generation (VG) from noble and transition metal-acidified solutions was performed after mixing acidified standards with sodium borohydride. Reagents were mixed inside the 100-μL reaction loop, and the evolved vapors formed were swept from the gas liquid separator to the ICP torch using a 0.7 L min⁻¹ Ar flow. Vapor generation and detection conditions using ICP-OES are summarized in Table I.

RESULTS AND DISCUSSION

Preliminary Experiments

Several surfactants were tested (SLS, SDBS, Aerosol-OT, and Triton-X100), all combined with Antifoam A (Antifoam B is an aqueous emulsion of Antifoam A), in concentrations lower, similar, and higher than their critical micellar concentration. However, in the conditions tested, only significant signals of noble and transition elements were obtained for CTAB without much

foaming. Therefore, CTAB was selected for further experiments because of the sensitivity and the simplicity of preparing the standards.

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 of 0.15 mg L⁻¹) were prepared for the following experiments, together with the reagent blanks. The 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.

TABLE I
Working Conditions for Vapor Generation Coupled to ICP-OES

Wavelength	
Ag	328.068 nm
Au	242.795 nm
Cd	214.440 nm
Cu	324.752 nm
Ni	231.604 nm
Sn	189.927 nm
Zn	213.857 nm
Power of plasma generator	1300 W
Outer Ar flow rate	15 L min ⁻¹
Injection Ar flow rate	0.7 L min ⁻¹
Intermediate Ar flow rate	0.5 L min ⁻¹
Viewing height	15 mm, Axial mode
Purge gas flow	Normal
Read delay	40 s
Replicates	5
Integration time	Auto
Sample flow rate	1.5 mL min ⁻¹
Sample flow/reductant flow ratio	1:1

CTAB: Optimization of Operational Variables

Optimization of Reductant Concentration

Variation in the corrected intensities was studied when using different concentrations of NaBH_4 [0.6% (w/v), 1.2 % (w/v), and 2.2% (w/v)]. Standards were prepared by diluting a portion of the stock standards in 0.6 M nitric acid, and using 2.5×10^{-5} M CTAB (11). The reductant was stabilized with 0.4% (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 Figure 1(a). It can be observed that the optimum concentration of sodium borohydride was 2.2% (w/v) for all elements. As in previous studies (2-4), the increase of sodium borohydride and of the amount of generated hydrogen had a positive effect on the generation of vapors from noble and transition metal

solutions. The increase on the reductant concentration has to be handled with care, as increments in noise (34) and carryover (21) of sodium in the plasma have been reported earlier. In this study, a concerning increase in the standard deviations was observed for cadmium with an increase in the reductant concentration. This fact might have led to the existence of memory effects for this analyte.

Selection of Acid and Optimization of Its Concentration

The acid concentration in the standards was optimized using 2.2% (w/v) sodium borohydride. Concentrations ranging from 0.3 to 0.7 M of nitric and hydrochloric acid were evaluated. Higher signals were obtained for all of the elements generating the vapors in nitric media, except for Ag. Therefore, nitric acid was selected to perform the following experiments. Normalized intensities for nitric acid are shown in Figure 1(b). Different optimum acidities for the various elements have been reported previously

(35,36). In this study, higher signals were obtained for all of the elements when using 0.6 M nitric acid, whereas maximum signal was obtained for Au at a 0.3 M concentration. A similar behavior was observed for hydrochloric acid.

Optimization of CTAB Concentration

Different concentrations of CTAB (1.25×10^{-5} M, 2.5×10^{-5} M, 5×10^{-5} M, and 10×10^{-5} M) were tested to generate the vapors. The standards were prepared in 0.6 M nitric acid and the corresponding amount of CTAB was added. A solution of 2.2% (w/v) sodium borohydride was used as the reductant agent. Optimization of CTAB concentration is shown in Figure 1(c). A concentration of 2.5×10^{-5} M of CTAB was selected as a compromise condition for the noble and transition metal determinations. This concentration is under the micellar critical concentration (0.9×10^{-3} M in water) and was the same as that used by Sun et al. (11) when determining Zn in milk powder and

Fig.1. Optimization of vapor generation using CTAB. (a) Concentration of sodium borohydride, (b) Concentration of nitric acid, (c) Concentration of CTAB, (d) Optimization of Ar flow.

wheat powder certified reference material (digested samples, 0.35 M hydrochloric acid, 0.8 mg L⁻¹ nickel in the standards).

Optimization of Argon Flow

Finally, the influence of the argon flow (0.6, 0.7, 0.8, and 0.9 L min⁻¹) was evaluated, and the results are shown in Figure 1(d). This parameter is connected with the release of the formed vapors from the liquid phase and with their transfer to the plasma. An argon flow value of 0.7 L min⁻¹ was selected for all elements. This argon flow was optimum for the detection of Ag, Au, and Cd, whereas higher signals were obtained for Cu, Sn, and Ni when a 0.8 L min⁻¹ argon flow was used. The different optimum Ar flow rates could also reflect processes in the plasma relevant to each metal. It has to be taken into account that the same

viewing height (15 mm) was used for all of the measurements.

Optimized Measurement Conditions

In conclusion, the optimum values of the parameters influencing the simultaneous vapor generation of Ag, Au, Cd, Cu, Ni, Sn, and Zn were as follows: NaBH₄ = 2.2% (w/v), HNO₃ = 0.6 M, CTAB = 2.5×10⁻⁵ M, argon flow = 0.7 L min⁻¹, sample flow/reductant flow ratio 1:1, sample flow and reductant flow of 1.5 mL min⁻¹, respectively.

CTAB and 1-butyl-3-methylimidazolium bromide: Optimization of Operational Variables

The combined performance of an ionic liquid (1-butyl-3-methylimidazolium bromide) with DDTC was used by Zhang et al. (24) as a reaction media modifier for increasing

the efficiency in vapor generation. Therefore, the effect of the addition of this compound was tested in the present study in combination with the optimized concentration of CTAB 2.5×10⁻⁵ M. The study was performed using hydrochloric or nitric acid in the reaction media at 0.15 M or 0.5 M concentration. Table II shows the blank-corrected intensities obtained in the experiments. The best results obtained are highlighted in bold type, and improvements can be observed on the sensitivity when both modifiers are combined. Better results for Au, Cd, Ni, and Sn were obtained using HNO₃; thus, we selected this acid to continue the optimization. The physical parameters were the same as those obtained for CTAB: sample flow/reductant flow ratio of 1:1, sample flow and reductant flow of 1.5 mL min⁻¹, respectively.

TABLE II
Corrected Emission Intensities Obtained Using the Ionic Liquid
1-Butyl-3-methylimidazolium Bromide (20 mM) in Acid Media and 2.5×10⁻⁵ M of CTAB

	Ag 328.068 nm		Au 242.795 nm		Cd 214.440 nm	
	<u>0.15 M</u>	<u>0.5 M</u>	<u>0.15 M</u>	<u>0.5 M</u>	<u>0.15 M</u>	<u>0.5 M</u>
HNO ₃	133.0	344.8	639.3	961.8	1593.1	9509.8
CTAB-HNO ₃	2330.5	5047.2	1872.0	2545.1	4891.7	17361.6
HCl	1565.7	2587.0	755.8	909.5	1291.7	2057.9
CTAB-HCl	5123.1	12962.9^a	1847.4	2298.9	3735.8	4253.9
	Cu 324.752 nm		Ni 231.604 nm		Sn 189.927 nm	
	<u>0.15 M</u>	<u>0.5 M</u>	<u>0.15 M</u>	<u>0.5 M</u>	<u>0.15 M</u>	<u>0.5 M</u>
HNO ₃	5606.7	7563.5	748.8	867.0	524.6	3142.6
CTAB-HNO ₃	14951.7	17535.3	2027.3	2740.1	422.2	3619.0
HCl	5973.8	6382.0	838.5	627.8	12.9	2552.3
CTAB-HCl	14927.6	16370.5	2334.4	1552.1	76.1	2466.7
	Zn 231.852 nm					
	<u>0.15 M</u>	<u>0.5 M</u>				
HNO ₃	1112.2	552.9				
CTAB-HNO ₃	2904.1	1772.7				
HCl	1146.9	1172.7				
CTAB-HCl	3074.3	2769.9				

^a Bold lettering indicates best results obtained.

Optimization of Reductant Concentration

Variation in the corrected intensities was studied when using different concentrations of NaBH_4 (0.75% (w/v), 1% (w/v), 1.5% (w/v), 2% (w/v), and 2.2% (w/v)). The standards were prepared by diluting a portion of the stock standards in 0.4 M nitric acid, and using 2.5×10^{-5} M CTAB and 20×10^{-3} M of ionic liquid. The reductant was stabilized with 0.4% (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 Figure 2(a). It can be observed that the optimum concentration of sodium borohydride was 2.2% (w/v) for most of the elements, with the exception of Cd and Sn.

Optimization of Nitric Acid Concentration

The acid concentration in the standards was optimized using 2.2% (w/v) sodium borohydride. Concen-

trations ranging from 0.3 to 0.7 M of nitric acid were studied. Normalized intensities for the elements when using nitric acid are shown in Figure 2(b). A concentration of 0.3 M nitric acid was selected to perform further experiments. However, the maximum signal was obtained for Cd when using 0.6 M nitric acid. This change on the optimum acidity can be explained by the effect of a new modifier on the reaction media.

Optimization of CTAB Concentration

Different concentrations of CTAB were tested to generate the volatile species. Standards were prepared in 0.4 M nitric acid and 20×10^{-3} M 1-butyl-3-methylimidazolium bromide. The corresponding amount of CTAB (0.75×10^{-5} M, 1.5×10^{-5} M, 2.5×10^{-5} M, 3.5×10^{-5} M, and 4.5×10^{-5} M) was added. A solution of 2.2% (w/v) sodium borohydride was used as a reductant agent. Optimization of the CTAB concentration is shown in Figure 2(c). In this case, the maximum signal for Cd was obtained with a con-

centration of CTAB of 4.5×10^{-5} M. However, a concentration of 1.25×10^{-5} M of CTAB was selected as a compromise condition for the noble and transition metal determinations.

Optimization of Ionic Liquid Concentration

The following ionic liquid concentrations were tested to determine Ag, Au, Cd, Cu, Ni, Zn, and Sn: 0, 12.5, 18.5, 25, 37.5, and 50×10^{-3} M. A concentration of CTAB of 1.25×10^{-5} M was added to all of the solutions. There was a combined effect of both modifiers for all elements when a concentration of 18.5×10^{-3} M of ionic liquid was added (Figure 2(d)), although not all of them exhibited an increase in sensitivity. In Figure 2(d), we observed how the normalized intensities for Ag, Au, and Sn do not seem to improve by adding the ionic liquid; yet they increased for Cd, Cu, Ni, and Zn. The increment was moderate for Cd (25%), Cu (12%), and Zn (35%), while Ni exhibited the highest increase in its signal intensity (51%).

Fig. 2. Optimization of vapor generation using CTAB + IL. (a) Concentration of sodium borohydride, (b) Concentration of nitric acid, (c) Concentration of CTAB, (d) Concentration of IL.

Analytical Performance of the System

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 of the standards had a concentration of 1 mg L⁻¹ of Co, 0.6 M of nitric acid, and 2.5×10⁻⁵ M of CTAB. The linearity of the calibration graphs was good ($r < 0.995$). Table III includes calibration graphs that were obtained using the vapor generation methods developed (with CTAB or IL+CTAB) and conventional nebulization (CN) (using a cyclonic spray chamber and Gem-Cone™ nebulizer, both from PerkinElmer, Inc.). In this case, the measurement conditions were: Ar

plasma flow: 15 L min⁻¹, auxiliary flow: 0.5 L min⁻¹, nebulizer Ar flow: 0.7 L min⁻¹; sample flow: 1.5 mL min⁻¹). In Table III, the calibration graphs show the relationship between “I” (the emission intensity) and the concentration of each element expressed in mg L⁻¹. As an example, the calibration graphs obtained for Ag, Au, Cd, Cu, Ni, and Zn using vapor generation with CTAB are shown in Figure 3.

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 and the methods of analysis (vapor generation with CTAB or IL+CTAB) are shown in Table III, together with the values obtained using conventional nebulization (CN). The detection limit for Ag using only CTAB was 14.3 µg L⁻¹, which is much higher than for conventional nebulization. This value can be improved by using different conditions: either a smaller CTAB concentration [Figure 2(c)] or using the combined effect of CTAB and 1-butyl-3-methylimidazolium-bromide with a LOD of 4.9 µg L⁻¹ for Ag. This approach seems to be much more suitable for Ag determination in the presence of other metals than the use of CTAB alone. For the remaining elements, the limits of detection were lower than 10 µg L⁻¹. For Au and Cu, the LODs obtained using CTAB were lower

TABLE III
Calibration Graphs and Analytical Performance of the VG-ICP-OES Method

	Method	Calibration Graphs	R	LOD (µg L ⁻¹)	LOQ (µg L ⁻¹)	RSD (%)
Ag 328.062 nm	CN ^a	I = 36090.0[Ag] + 79.3	1.000	2.7	9.09	5.4
Ag 328.062 nm	CTAB	I = 22102.3 [Ag] + 5801.2	0.999	14.3	47.6	2.8
Ag 328.062 nm	IL+CTAB	I = 27637.2 [Ag] + 2291.3	0.999	4.9	16.4	2.7
Au 242.795 nm	CN	I = 3333.9 [Au] - 514.2	0.995	12.0	41.0	2.4
Au 242.795 nm	CTAB	I = 8047.3 [Au] + 153.0	0.998	6.9	23.0	2.6
Au 242.795 nm	IL+CTAB	I = 4122.4 [Au] + 58.293	0.999	14.1	7.4	3.3
Cd 214.440 nm	CN	I = 14088.0[Cd] - 0.9	1.000	0.86	2.7	0.8
Cd 214.440 nm	CTAB	I = 53478.6[Cd] + 790.3	0.998	1.0	3.3	11.3
Cd 214.440 nm	IL+CTAB	I = 15569.4[Cd] - 186.64	0.999	2.0	6.8	9.2
Cu 324.752 nm	CN	I = 94114.0 [Cu] + 517.3	1.000	1.1	3.6	2.0
Cu 324.752 nm	CTAB	I = 114625.5 [Cu] - 808.6	0.999	0.45	1.4	4.0
Cu 324.752 nm	IL+CTAB	I = 54072.9 [Cu] - 796.1	0.996	2.7	8.9	2.8
Ni 231.604 nm	CN	I = 7315.3[Ni] + 19.4	1.000	2.6	8.8	1.8
Ni 231.604 nm	CTAB	I = 7427.2[Ni] - 1.4	0.998	6.1	20.3	4.0
Ni 231.604 nm	IL+CTAB	I = 4173.5 [Ni] - 147.68	0.996	5.4	18.0	4.3
Sn 189.927 nm	CN	I = 264.1[Sn] - 3.4	0.996	28.2	94.2	40.6
Sn 189.927 nm	CTAB	I = 15151.6 [Sn] + 51.3	0.999	1.5	4.8	4.6
Sn 189.927 nm	IL+CTAB	I = 3921.2 [Sn] + 44.296	0.999	6	12.2	2.5
Zn 213.857 nm	CN	I = 8175.7 [Zn] + 71.6	1.000	1.4	4.5	0.9
Zn 213.857 nm	CTAB	I = 8680.1 [Zn] - 38.3	0.998	2.8	9.3	2.9
Zn 213.857 nm	IL+CTAB	I = 7618.8 [Zn] - 102.4	0.998	5.7	19	9.7

^a CN = conventional nebulization.

than those obtained using conventional nebulization (Au: $6.9 \mu\text{g L}^{-1}$ vs. $12.0 \mu\text{g L}^{-1}$; Cu: $0.45 \mu\text{g L}^{-1}$ vs. $1.1 \mu\text{g L}^{-1}$).

In this system, the volatile species are transported to the plasma torch using a 1-mm i.d. transfer line. When the samples were introduced using pneumatic nebulization, the analyte was introduced using a cyclonic chamber with a much wider inner diameter. It was observed that the optimum alignment of the plasma torch was different for vapor generation and conventional nebulization, and it had an effect on the sensitivity. Therefore, the torch was aligned using 10 mg L^{-1} Mn for pneumatic mobilization and 10 mg L^{-1} of Sn for chemical vapor generation.

The best limits of detection in the literature have a value of approximately $1 \mu\text{g L}^{-1}$ using VG-ICP-OES instrument. We obtained a limit of detection of $0.4 \mu\text{g L}^{-1}$ for copper, lower than the value of $0.7 \mu\text{g L}^{-1}$ as obtained by Duan et al. (36). Xu et al. (37) obtained a similar result using o-phenantroline and acetic acid as a reaction media, but the calibration graphs were lineal only up to 0.2 mg L^{-1} .

In the literature concerning chemical vapor generation of the noble and transition elements using sodium tetrahydroborate as the reductant agent, there are just a few reports published for the simultaneous determination of several elements (2-4, 34, 36, 38, 39). However, there is an increasing interest

in the simultaneous determination of hydride-forming elements and non-hydride-forming elements using spray chambers as the gas liquid separator (40). There are also special commercial devices designed such as the Multimode Introduction System (41-44) or the Concomitant Metal Analyzer (45,46). The present method can be used to measure simultaneously seven elements, and could be modified also to improve the performance of the individual elements using the optimum conditions for each element.

The improvement of the Cu detection limit is surprising. We think that a possible explanation of the success of this method for Cu might be the control on the nanoparticle sizes by CTAB. Chen

Fig. 3. Calibrations graphs obtained for Ag, Au, Cd, Cu, Ni, and Zn using vapor generation with the CTAB modifier.

et al.(47) reported using sodium borohydride and a $1-2 \times 10^{-3}$ M CTAB reaction medium to control the size of the copper-generated nanoparticles (2–10 nm). The use of CTAB for copper determination seems to be a promising approach and might be interesting to explore separately.

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}). The average intensities, standard deviations, and relative standard deviations (%RSDs) were calculated. The obtained RSD values for the selected lines for the different elements are listed in Table III. The elements Ag, Au, Cu, Ni, Sn, and Zn showed RSD values lower than 5%. The RSD for Ag (2.8%) was lower than for conventional nebulization (5.4%). The RSD value for Cd was the only one above 10% (11.3%), probably due to memory effects.

The formation of an aerosol carrying nanoparticles has been proven for Ag (51) and Au (22). The lack of control of their size distribution and introduction on the

ICP might affect the measurements. In recent years, different devices such as a slurry nebulizer (48) or a microdroplet generator (49) have been employed for single particle detection with ICP-MS. This might be an important factor to explore/control in the future.

Interference Study for the CTAB Method

Since the best results were obtained for most of the elements using only CTAB, possible interferences of this approach were studied. Sun et al. (11) reported that CTAB was a reagent which could avoid numerous interferences in Zn determination by VG-AFS. Therefore, we performed a study to evaluate if CTAB could diminish interferences under the optimized vapor generation conditions. Therefore, 2 mg L^{-1} and 10 mg L^{-1} of interferences were prepared in standard solutions containing 0.15 mg L^{-1} of each element (except for Sn: 0.05 mg L^{-1}). In a previous study (2), we had found that nickel and copper were the main interferences to generate vapors from noble and transition metal solutions if 8-hydroxyquinoline was used as the modifier. These two elements

were also found to be troublesome in terms of interferences as reported by Pohl et. al. (50). In the present paper, Ni and Cu were tested as interferences together with Co, Zn, Fe, and Pb. The effect on the signals is shown in Table IV. The values were calculated after three measurements of each standard with and without the interferences. The best recoveries of the elements were obtained using CTAB in comparison with the use of 8-hydroxyquinoline (2), especially at the 2 mg L^{-1} level. To completely avoid the presence of interferences, it would probably be necessary to increase the CTAB/metal concentration ratio to cope with the higher amount of ions present in the solution (3).

Accuracy

The certified reference material for measurement of the elements in wastewater (SPS-WW2 Batch 110, Spectrapure Standards, Oslo, Norway) containing Cd, Cu, Ni, and Zn was analyzed to test the accuracy of the measurements. Application of the method was not as straightforward as desired. Cd, Cu, and Ni were successfully measured using an aqueous calibration and a dilu-

TABLE IV
Percentage Recoveries of the Signal After Interferent Addition

	Au 242.795 nm	Ag 328.068 nm	Cu 324.752 nm	Cd 214.440 nm	Ni 231.604 nm	Sn 189.927 nm	Zn 213.857 nm
2 mg L ⁻¹ Co	97.9	148.9	107.1	101.9	92.0	59.4	92.3
10 mg L ⁻¹ Co	58.7^a	93.1	63.7	100.7	46.0	55.3	44.8
2 mg L ⁻¹ Cu	102.0	101.4		52.2	96.8	43.7	97.9
10 mg L ⁻¹ Cu	39.9	50.2		28.5	58.9	42.8	74.4
2 mg L ⁻¹ Zn	95.6	90.9	109.2	100.1	102.3	91.3	
10 mg L ⁻¹ Zn	94.3	71.0	110.0	76.4	58.6	101.4	
2 mg L ⁻¹ Ni	102.7	92.6	99.5	73.4		63.3	107.8
10 mg L ⁻¹ Ni	60.4	56.4	44.8	24.2		20.2	50.3
2 mg L ⁻¹ Fe	100.9	92.9	88.0	100.6	101.6	96.8	82.7
10 mg L ⁻¹ Fe	105.1	104.4	64.6	95.1	110.6	93.4	66.8
2 mg L ⁻¹ Pb	95.3	101.0	95.5	73.6	91.5	83.6	92.6
2 mg L ⁻¹ Pb	91.5	102.2	103.7	44.7	83.8	102.4	26.8

^a Bold lettering represents values of < 90%.

tion of the sample of 2 mL to 25 mL Cu and Zn or 2 to 10 Cd in the reaction media. A standard addition calibration curve ranging from 0 to 0.5 mg L⁻¹ was used to determine Zn (sample dilution 0.85 mL to 10 mL). The obtained values showed good agreement with the certified contents of the material (Table V). Taking into account the concentration ratios of Cd, Cu, and Ni on the samples, the simultaneous Cd determination with the other elements was not possible. When a 2 to 10 dilution factor was employed, Cd could be successfully determined and interference from the other elements was avoided, even though the deviations were higher than for the other elements. This behavior reported here might have to do with the nature of the volatile metallic species (15,22,51).

CONCLUSION

Variables influencing the simultaneous determination of Ag, Au, Cd, Cu, Ni, Sn, and Zn by VG-ICP-OES in a surfactant reaction medium such as cetyl trimethyl ammonium bromide (CTAB) have been optimized in the present work. The limits of detection ranged from 0.4 µg L⁻¹ (Cu) to 6.9 µg L⁻¹ (Au), except for Ag (14.3 µg L⁻¹). The relative standard deviations were below 5% (n=11) for all of the elements, except for Cd (11.3%). A study of interferences was performed which confirmed that CTAB is a compound that can reduce interferences better than other reaction media modifiers, such as 8-hydroxyquinoline. The method was applied successfully to the determination of Cu, Cd, Ni, and Zn in a wastewater certified reference material. The changes on vapor generation due to the combined effect of CTAB and 1-butyl-3-methylimidazolium bromide were confirmed during the optimization process. This mixed modifier offers a 3-fold improvement in the detection limits for Ag.

TABLE V
Accuracy: Analysis of the SPS-WW2 Certified Reference Material

Elements	Certified Concentration (µg L ⁻¹)	Experimental Concentration (µg L ⁻¹)
Cd	100.0 ± 0.5	102.9 ± 1.2
Cu	2000 ± 10	1962.0 ± 112.0
Ni	5000 ± 25	4964.0 ± 121.0
Zn	3000 ± 15	3040.4 ± 210.8

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