Use of DDTC or O-phenanthroline as Reaction Media Modifiers for the Simultaneous Determination of Au, Cd, Cu, Ni, Sn, and Zn by VG-ICP-OES

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INTRODUCTION

Several types of reagents [e.g., surfactants (1-4) and metallic catalysts (2,4-7)] have been used as reaction media modifiers to increase the efficiency of the reaction of vapor generation. Donor species and oxidizing or reducing species added to the reaction media to enhance vapor generation can greatly influence the generation of volatile compounds by modifying the structure of the coordination sphere of the analyte through complex formation (8).

The main complexing agents used for the generation of vapors from transition and noble elements are 8-hydroxyquinoline, diethyldithiocarbamate (DDTC), and o-phenanthroline. The modifier 8-hydroxyquinoline was used for determining zinc and cadmium by atomic fluorescence spectrometry (AFS) (7) coupled with an intermittent flow generation system. It was also used for multielemental determination of noble and transition elements by inductively coupled plasma optical emission spectrometry (ICP-OES) (9,10) and high resolution continuum source atomic emission spectrometry (HRCS-AAS) (11).

Diethyldithiocarbamate (DDTC) was first used to assist the generation of volatile cadmium species in an organic medium (N,N'-dimethylformamide) for their atomic absorption spectrometry determination in a quartz tube (12). However, more

ABSTRACT

The objective of this work was to optimize the conditions for the simultaneous determination of Au, Cd, Cu, Ni, Zn, and Sn by VG-ICP-OES (vapor generation-inductively coupled plasma optical emission spectrometry) using diethyldithiocarbamate (DDTC) or o-phenanthroline as reaction media modifier. A univariate procedure was used to select the working conditions (Ar flow, flow rates for sample, reductant and waste, and reagent concentrations). The optimum nitric acid concentration was 0.4M when using o-phenanthroline or 0.5M when using DDTC. The modifier concentration was 3.5 mg/L (o-phenanthroline) or 0.005% (w/v) DDTC. The optimum sodium borohydride concentration was 2.24% (w/v) + 0.4% (w/v) NaOH, argon purge flow to sweep the vapors to the torch 0.7 L/min, sample to reductant ratio 1:1, sample flow and sodium borohydride flow 2.0 mL/min for o-phenanthroline and 1.5 for DDTC mL/min, and the waste flow rate 7.7 mL/min. The limits of detection were lower than those obtained using conventional nebulization, except for Cu and Ni. With DDTC, the best limits of detection were for Au (3.6 µg/L) and Cd (0.53 µg/L); whereas for o-phenanthroline, the best limits of detection were obtained for Au (3.7 µg/L), Cu (2.5 µg/L), Ni (4.9 µg/L), Sn (1.1 µg/L), and Zn (0.98 µg/L). These LODs were better than those obtained with 8-hydroxyquinoline in the same vapor generation system, except for Ni. The measurements were precise (RSDs ≤ 10% for Au, Cd, Ni, Sn, and Zn; for Cd: 11.0-11.4%).

literature using this reagent is also devoted to gold determination. Du et al. (13,14) observed that DDTC in sample solution was an efficient enhancement reagent for vapor generation of gold (optimum concentration 0.03%). These authors achieved a sensitivity enhancement factor of 21 using a flow injection vapor generation atomic absorption spectrometry system (FI-VG-AAS) with a quartz tube atomizer. In another study, they used microamounts of DDTC and Pd (6) for preconditioning the reaction coil inner wall and the gas-liquid separator in the generation of gold vapors. Those vapors were trapped *in situ* on a graphite tube inner wall for electrothermal atomic absorption spectrometry (ETAAS) detection, and for determining the element in ore sample digests. DDTC was also used to quantify Au in geological certified reference materials (4 soil and 4 gold ore samples) by VG-AFS (15). Xu and Sturgeon (16) used a mixed reductant (0.1% sodium borohydride + 0.01% sodium tetraethylborate) for vapor generation of gold in the presence of 0.03% DDTC. In the absence of DDTC, almost no signal was observed, and the presence of low concentrations of tetraethylborate enhanced the sensitivity 8-fold, making possible the determinations in a quartz tube atomizer. In recent studies, room temperature ionic liquids have been used for assisting vapor generation of noble and transition metals (17,18). Zhang et al. (19) found a synergetic enhancement effect of the combined use of 1-butyl-3-methylimidazolium bromide (25 mmol/L) and DDTC (0.02%) as reaction media modifiers in the determination of Ni by VG-AFS. The

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surfactant Triton® X-100 and Antifoam B have also been used together with DDTC to generate vapors of Au in a flow injection system coupled with a quartz tube multi-atomizer for atomic absorption spectrometry (20). A similar compound, ammonium pyrrolidine dithiocarbamate (APDC), was used as enhancer of Ni and Co vapor generation (22), and in combination with room temperature ionic liquids to improve vapor generation of Zn (22), Fe, Co, and Ni (23).

The modifier o-phenanthroline was more efficient in the generation of vapors of other elements such as copper (o-phenanthroline concentration in sample solution: 0.00048%) (14), detected by FI-VG-AAS with a 10-fold enhancement factor. Sun et al. (24) used nickel combined with o-phenanthroline (optimum concentration 12 µg/L) as enhancement reagents in the determination by VG-AFS of total Zn, water-soluble Zn and n-octanol-soluble Zn in Chinese herbal medicines. Sun and Suo (7) determined Cd and Zn simultaneously using AFS, and evaluated different complexant reagents: o-phenanthroline, 8-hydroxyquinoline, ferron, thiourea, EDTA, ascorbic acid, L-cystein, and a surfactant (CTAB). The modifiers 8-hydroxyquinoline, o-phenanthroline, and CTAB increased the signals 11.9-fold, 12.1-fold, and 6.2-fold for Zn, and 7.3-fold, 6.7-fold and 5.6-fold for Cd, respectively. Concentrations of approximately 1 mg/L of Co or Ni had a synergistic effect on the enhancement of the reaction efficiency.

The objective of the present study was to optimize the operating conditions for the simultaneous determination of noble and transition metals (Au, Cd, Cu, Sn, Zn, and Ni) using DDTC or o-phenanthroline as reaction media modifier and to determine the elements by inductively coupled plasma optical emission spectrometry.

EXPERIMENTAL

Instrumentation

An Optima™ 3300 DV ICP-OES (PerkinElmer, Shelton, CT, USA) was used to determine noble and transition metals. The spectrometer system includes a three-channel software-controlled peristaltic pump. The vapor generation system consists of a 100 µL reaction loop and a home-made forced outlet gas-liquid separator connected directly to the torch base using a 60 cm PTFE tube and a 4 cm Tygon® tube (9) (PTFE tubing: 0.5 mm i.d.). The nebulization argon provided by the equipment was used to purge the sample and transport the vapors directly into the ICP torch. A Minipuls™ 3 Peristaltic Pump (Gilson, Villiers-le-Bel, France) was used to pump the liquid waste from the outlet of the gas-liquid separator (Figure 1).

The performance of this system was compared with conventional sample introduction using a cyclonic chamber and a GemCone™ nebulizer (PerkinElmer, Inc., Shelton, CT, USA).

Standard Solutions and Reagents

Stock solutions of 1000 mg/L amounts were purchased from different suppliers: BDH, Poole, UK (Co, Ni, Ag, Sn); Fluka, Steinheim, Switzerland (Au); Merck, Darmstadt, Germany (Cd, Zn), and PerkinElmer, Inc., Shelton, CT, USA (Cu).

The following reagents were used to generate vapors: Nitric acid 69% (w/v) or hydrochloric acid 35% (w/v) (hyperpure), 1,10-phenanthroline 1-hydrate (PA-ACS) from Pan-reac SA (Barcelona, Spain), sodium diethyl-dithiocarbamate trihydrate (DDTC) from Merck (Steinheim, Switzerland), and NaBH₄ (Avocado Research Chemicals Ltd, Heysham, UK) stabilized with NaOH, GR for analysis, ACS, Reag. Ph. Eur. from Merck (Darmstadt, Germany).

All solutions were prepared with ultrapure water, with a specific resistance of 18 MΩ/cm, obtained from a Milli-Q™ purification system (Millipore Corporation, USA). All glassware and material was cleaned using ultrapure water, kept in 10% nitric acid for 48 hours, and rinsed with ultrapure water. Afterwards, the material was stored dry and kept covered prior to use.

Fig. 1. Vapor generation and ICP-OES system.

The SPS-WW2 reference material for measurement of the elements in wastewaters (Spectrapure Standards, Oslo, Norway) was used to check the accuracy in the determination of Cd, Cu, Ni and Zn.

Procedures

Preparation of Standard Solutions

The standards were prepared by adding different concentrations of the elements (Au, Cd, Cu, Ni, Sn, Zn, and also Ag) to solutions containing the reaction media modifier, nitric acid and 1 mg/L of Co. A concentration of 3.5 mg/L (o-phenanthroline) or 0.005% (w/v) DDTC provided the maximum compromise sensitivity in the simultaneous determinations. The optimum con-

centration of nitric acid was 0.4 M and 0.5 M for o-phenanthroline and DDTC, respectively.

Metal Determination Using VG-ICP-OES

Vapor generation was performed by mixing acidified standards or samples with 2.24% (w/v) NaBH₄, stabilized with 0.4% (w/v) NaOH. The reagents were pumped using the Optima™ PerkinElmer® peristaltic pump, and waste was eliminated using the Minipuls™ 3 pump (Figure 1). The determinations were performed using the conditions listed in Table I. A 40-second read delay was used to allow transport of the reagents to the liquid-gas separator and to obtain a stable signal.

TABLE I
Operating Parameters for VG-ICPOES

Vapor Generation		
Modifier	o-phenanthroline	DDTC
Modifier concentration	3.5 mg/L	0.005% (w/v)
NaBH ₄ in 0.4% (w/v) NaOH	2.24% (w/v)	2.24% (w/v)
HNO ₃	0.4 M	0.5 M
Sample reductant ratio	1:1	1:1
Sample and reductant flows	2 mL/min	1.5 mL/min
Operating Parameters for ICP-OES Detection		
Element	Wavelength	
Ag	328.068 nm	
Au	242.795 nm	
Cd	214.440 nm	
Cu	324.762 nm	
Ni	231.604 nm	
Sn	189.927 nm	
Zn	213.857 nm	
Power of plasma generator	1350 W	
Outer Ar flow rate	15 L/min	
Purge Ar flow rate	0.7 L/min	
Intermediate Ar flow rate	0.5 L/min	
Viewing height	15 mm Axial mode	
Purge gas flow	Normal	
Read delay	40 s	
Replicates	4	
Integration time	5 s	

RESULTS AND DISCUSSION

O-phenanthroline: Optimization of Operational Variables

The variables affecting vapor generation of Au, Cd, Cu, Ni, Sn, and Zn were optimized in a univariate way, and Ag was also included in the study. The standard solutions for optimization contained 0.45 mg/L of Ag, Au, Cd, Cu, Ni, Sn, and Zn, and 0.15 mg/L of Sn. A concentration of 2 mg/L of o-phenanthroline and 1 mg/L of Co prepared in 0.4 M nitric acid in the standards was chosen as a reaction media to start the optimization of the operational variables.

Optimization of Sodium Borohydride Concentration

For these experiments, the standard solutions and blanks were mixed with reductant solutions of concentrations 0.6, 1.2, and 2.24% (w/v) in 0.4% (w/v) NaOH. The results in Figure 2 show that the higher the amount of reductant, the higher the signal obtained for all of the elements, except for Cd. Therefore, a concentration of 2.24% (w/v) sodium borohydride stabilized with 0.4% (w/v) NaOH was used in the following experiments.

Selection of Type of Acid and Optimization of its Concentration

The standard solutions and blanks were prepared containing 2 mg/L of o-phenanthroline and 1 mg/L of Co, and the following concentrations of nitric acid or hydrochloric acid were tested: sodium borohydride 0.2 M, 0.3 M, 0.4 M, 0.5 M, 0.6 M, and 0.7 M. 2.24% (w/v) with 0.4% (w/v) of NaOH was used to generate the vapors. Nitric acid provided the highest signals for Cd (1.4x), Cu (1.2x), and Ni (1.5x), and hydrochloric acid for Ag (5.4x) and Sn (3x). The results were similar for

Au and Zn. Therefore, nitric acid was chosen as the reaction media. The results of the optimization of nitric acid concentration are shown in Figure 3. Nitric acid of 0.4 M was the compromise value selected to carry out the following measurements because it was the optimum concentration value for Ag, Au, Cu, Ni, and Sn. The optimum values for Zn were 0.30.4 M nitric acid and for Cd 0.6 M nitric acid.

Optimization of O-phenanthroline Concentration

Standard solutions and their respective blanks, prepared in 0.4 M of HNO_3 with 1 mg/L of Co and different concentrations of o-phenanthroline (0.0, 0.2, 0.5, 1.0, 2.0, 3.5, 5.0, and 6.5 mg/L), were mixed with 2.24% (w/v) sodium borohy-

dride stabilized with 0.4% (w/v) NaOH. The signals increased at higher concentrations of o-phenanthroline, reaching a plateau at 3.5 mg/L (Figure 4), which was the concentration selected for subsequent experiments.

Optimization of Ar Purge Flow

A standard solution and a blank containing 0.45 mg/L of each metal (and 0.15 mg/L of Sn, plus 1 mg/L of Co, 3.5 mg/L of o-phenanthroline, and 0.4 M nitric acid) were mixed with 2.24% (w/v) sodium borohydride, stabilized with 0.4% (w/v) NaOH. The influence of the Ar purge flow in signal intensities (corrected with corresponding blanks) was studied, and the normalized results for all of the elements are shown in Figure 5.

The Ar flow selected to sweep the vapors to the torch was 0.7 L/min (compromise value).

Sample and Reductant Flows

The effect of increasing the sample flow:reductant flow ratio from 1:1 to 1.5:1 was tested. The ratio 1:1 provided the best signals for all of the elements, with the exception of Sn and Au, which showed comparable values for both ratios. The use of the same flow of sample and reductant is especially important in the case of Ni and Zn, because the signals are 4 or 8 times higher, respectively. When acid concentration is higher than 0.5 M, it is not possible to use sample and reductant flows higher than 1.5 mL/min because the plasma becomes unstable. However, if the

Fig. 2. Optimization of the sodium borohydride concentration used for vapor generation: (a) o-phenanthroline as modifier and (b) DDTC as modifier.

Fig. 3. Optimization of nitric acid concentration for vapor generation using: (a) o-phenanthroline (b) DDTC.

Fig. 4. Optimization of modifier concentration for vapor generation: (a) o-phenanthroline and (b) DDTC.

Fig. 5. Optimization of carrier Ar flow: (a) o-phenanthroline and (b) DDTC.

Fig. 6. Influence of sample and reductant flow in vapor generation using o-phenanthroline as reaction media modifier.

nitric acid concentration is lower than 0.5 M, the sensitivity can be improved by increasing the flow rates. Therefore, experiments were carried out to optimize the flows of sample and reductant (flows studied: 1.5 mL/min, 1.75 mL/min, 2.0 mL/min, and 2.25 mL/min). The compromise flow selected as optimum was 2.0 mL/min (Figure 6).

The optimum conditions for the simultaneous generation of vapors from Ag, Au, Cd, Cu, Ni, Sn, and Zn, using sodium borohydride as a reductant and o-phenanthroline as a reaction media modifier, are listed in Table I.

DDTC: Optimization of Operational Variables

A concentration of 0.01% (w/v) DDTC and 1 mg/L of Co and 0.4 M nitric acid in the standards (0.45 mg/L of Ag, Au, Cd, Cu, Ni and Zn, 0.15 mg/L of Sn) were chosen to start the optimization of the operational variables affecting the vapor generation of those elements.

Optimization of Sodium Borohydride Concentration

For these experiments, a standard solution and a blank were mixed with reductant solutions of concentrations 0.6, 1.2, and 2.24% (w/v) in 0.4% (w/v) NaOH. The results in Figure 2 show that the higher the amount of reductant, the higher the signal obtained for all of the elements, except for Sn. Therefore, a concentration of 2.24% (w/v) sodium borohydride stabilized with 0.4% (w/v) NaOH was used for the following experiments.

Selection of Type of Acid and Optimization of its Concentration

Standard solutions and blanks were prepared containing 0.01% (w/v) DDTC and 1 mg/L of Co, and the following concentrations of nitric acid or hydrochloric acid were tested: 0.2 M, 0.3 M, 0.4 M, 0.5 M, 0.6 M, and 0.7 M. Sodium borohydride at a concentration of 2.24% (w/v) with 0.4 % (w/v) NaOH was used to generate the vapors. Nitric acid provided the highest signals for Au (1.2x), Cd (1.9x), Ni (2.2x), Sn (9x), and Zn (1.8x), while hydrochloric acid provided the highest signals for Ag (4.8x). Both acids provided comparable results for Cu. Therefore, nitric acid was chosen as a reaction media for the simultaneous determination of the elements. The results of the optimization of nitric acid concentration are shown in Figure 3, and a concentration of 0.5 M was the compromise value selected to perform the determinations, which

was a slightly higher concentration than was selected for DDTC (0.4 M nitric acid).

Optimization of DDTC Concentration

After selecting the reductant and the nitric acid concentration in the samples, the optimization of the concentration of DDTC was carried out. Standard solutions were prepared containing a final concentration of 0.5 M nitric acid, 1 mg/L Co, the elements (1 mg/L of Ag, Au, Cd, Cu, Ni, and Zn, 0.25 mg/L of Sn), and the following concentrations of DDTC: 0, 0.001, 0.005, 0.01, 0.02, 0.03, 0.04 and 0.05 % (w/v). A concentration of 0.005% (w/v) DDTC was selected to be present as the modifier of the reaction media (Figure 4).

Optimization of Ar Purge Flow

A standard solution and a blank containing 0.45 mg/L of each metal [and 0.15 mg/L of Sn, plus 1 mg/L of Co, 0.005% (w/v) DDTC and 0.4 M nitric acid] were mixed with 2.24% (w/v) sodium borohydride, stabilized with 0.4% (w/v) NaOH. The influence of the Ar purge flow on the signal intensities (corrected with the blank) was studied, and the normalized results for all of the elements are shown in Figure 5. The Ar flow selected to sweep the vapors to the torch was 0.7 L/min (compromise value), and was not varied with the different modifiers (o-phenanthroline or 8-hydroxyquinoline) (9). This value could thus be mainly related to the physical characteristics of the vapor generation system.

Sample Flow : Reductant Flow Ratio

The effect of increasing the sample flow : reductant flow ratio from 1:1 and 1.5:1 was studied, but no significant differences between the two options were observed.

The optimum conditions for the simultaneous generation of vapors from Ag, Au, Cd, Cu, Ni, Sn, and Zn using sodium borohydride as the reductant and DDTC as the reaction media modifier are listed in Table I.

Influence of Addition of an Ionic Liquid

The ionic liquid 1-butyl-3-methylimidazolium bromide combined with DDTC was used by Zhang et al. (19) as a reaction media modifier for increasing the efficiency in vapor generation. Therefore, this compound at the optimum concentration selected by Zhang (25 mmol/L) was tested in combination with the optimized concentration of o-phenanthroline (3.5 mg/L), DDTC [0.005% (w/v)], and 8-hydroxyquinoline (38 mg/L) (9). The study was performed using hydrochloric or nitric acid in the reaction media and at 0.15 M or 0.5 M concentrations. Table II lists the corrected intensities obtained in the experiments. The best results obtained are highlighted in bold. It can also be seen that there were only increases in the signals for Cd with 8-hydroxyquinoline and o-phenanthroline, and for Zn using 8-hydroxyquinoline.

ANALYTICAL PERFORMANCE

Calibration Curves

Standard solutions each of 0, 0.075, 0.15, 0.30, 0.45, 0.6 and 0.75 mg/L for Ag, Au, Cd, Cu, Ni, Sn, and Zn (and 0, 0.025, 0.05, 0.10, 0.15, 0.20 and 0.25 mg/L of Sn) were prepared for calibration together with the corresponding amount of Co, nitric acid, and the modifier. Table III lists the slopes of the calibration graphs (sensitivities) and regression coefficients obtained in the optimum working conditions for each modifier.

For Ag, the response curves were not linear in the concentration range studied for DDTC or o-phenanthroline (vapors of Ag

Table II
Corrected Emission Intensities using the Ionic Liquid 1-Butyl-3-Methylimidazolium Bromide (20 mM)
in Acid Media and Mixed with Other Modifiers

Ag 328.068 nm			Au 242.795 nm		Cd 214.440 nm	
Modifier	0.15 M	0.5 M	0.15 M	0.5 M	0.15 M	0.5 M
HNO ₃	133.0	344.8	639.3	961.8	1593.1	9509.8
8HQ/HNO ₃	1060.0	295.2	847.1	904.3	3759.9	11382.2
DDTC/HNO ₃	2812.4	100.0	738.2	462.6	7594.2	973.2
o-phen/HNO ₃	248.3	17.4	626.1	488.0	2579.0	11585.7
HCl	1565.7	2587.0	755.8	909.5	1291.7	2057.9
8HQ/HCl	1901.3	2664.0	665.1	826.8	1043.6	2605.9
DDTC/HCl	3273.9	1356.8	892.3	343.1	1209.3	1169.6
o-phen/HCl	1830.2	2120.1	507.9	397.3	1510.9	1434.1

Cu 324.752 nm			Ni 231.604 nm		Sn 189.927nm	
Modifier	0.15 M	0.5 M	0.15 M	0.5 M	0.15 M	0.5 M
HNO ₃	5606.7	7563.5	748.8	867.0	524.6	3142.6
8HQ/HNO ₃	5684.3	7060.3	815.7	1212.1	1400.6	3142.3
DDTC/HNO ₃	3822.1	5033.9	805.9	607.1	3030.5	2090.0
o-phen/HNO ₃	5853.9	5023.8	1035.3	1263.5	1040.6	3333.3
HCl	5973.8	6382.0	838.5	627.8	12.9	2552.3
8HQ/HCl	4483.9	5589.6	591.9	655.1	516.3	2700.2
DDTC/HCl	2313.2	1378.3	355.0	276.5	1149.1	1546.8
o-phen/HCl	5678.7	4294.9	954.0	595.4	1250.5	2910.1

Zn 231.852 nm		
Modifier	0.15 M	0.5 M
HNO ₃	1112.2	552.9
8HQ/HNO ₃	846.8	942.7
DDTC/HNO ₃	685.3	1259.2
o-phen/HNO ₃	1671.2	573.7
HCl	2904.1	1772.7
8HQ/HCl	1146.9	1172.7
DDTC/HCl	783.8	1580.0
o-phen/HCl	1315.0	582.8
HNO ₃	1588.3	1313.9
8HQ/HNO ₃	3074.3	2769.9

were more easily generated in hydrochloric acid media than in nitric acid). In the case of DDTC, the calibration curves for Au, Cu, and Cd were linear up to 0.6 mg/L, and for Ni and Zn up to 0.45 mg/L. However, the linear range goes up to 0.45 mg/L when using o-phenanthroline. This range is similar to that obtained for 8-hydroxyquino-

line (linearity up to 0.6 mg/L) (9). These short linear ranges could be due to the change in the metal : modifier ratio concentration. If the volatile species were nanoparticles, the metal : modifier ratio concentration could affect their distribution size, and if the nanoparticles were large, they could have more difficulty in being released into the

aerosol for transport to the torch. This fact could explain the need of increasing the amount of 8-hydroxyquinoline to determine metals in steels in comparison with aqueous standards, and also the increase in the linear range of the method (the rise in metal concentration does not have much effect on the metal : modifier ratio concentration) (10).

Table III
Comparison of Analytical Performances

	Slope	r	LOD ($\mu\text{g/L}$)	LOQ ($\mu\text{g/L}$)	RSD (%)
Ag (328.062 nm)					
Conv. nebulization	36090.0	1.000	2.7	9.09	5.4
o-phenanthroline	Non-linear				
DDTC	Non-linear				
Au (242.795 nm)					
Conv. nebulization	3333.9	0.995	12.0	41.0	2.4
o-phenanthroline	15831.2	0.999	3.7	12.2	5.5
DDTC	10498.1	0.998	3.6	12.0	2.8
Cd (214.440 nm)					
Conv. nebulization	14088.0	1.000	0.86	2.7	0.8
o-phenanthroline	46974.4	0.995	1.1	3.6	11.0
DDTC	40200.4	0.996	0.53	1.7	11.4
Cu (324.752 nm)					
Conv. nebulization	94114.0	1.000	1.1	3.6	2.0
o-phenanthroline	107882.5	0.997	2.5	7.5	8.7
DDTC	69878.6	0.999	4.1	14	4.1
Ni (231.604 nm)					
Conv. nebulization	7315.3	1.000	2.6	8.8	1.8
o-phenanthroline	12432.0	0.999	4.9	15.6	5.4
DDTC	9256.5	0.999	6.1	20.3	1.9
Sn (189.927 nm)					
Conv. nebulization	264.1	0.996	28.2	94.2	40.6
o-phenanthroline	20960.6	0.999	1.1	3.8	7.9
DDTC	17448.3	0.999	3.2	10.6	2.7
Zn (213.857 nm)					
Conv. nebulization	8175.7	1.000	1.4	4.5	0.9
o-phenanthroline	13711.8	0.997	0.98	3.7	6.3
DDTC	15418.0	0.998	1.6	5.3	2.1

Fig. 7. Mechanisms involved in vapor generation of noble and transition metals.

The linear range is similar for the additives studied, which could mean that vapor generation reactions always create the same products regardless of the modifier used.

Feng et al. (25) analyzed the complex mechanisms involved in vapor generation of noble and transition metals. In the case of hydride-forming elements, the analyte

species (ML_n) are converted to the final stable hydride (MH_n) through the stepwise replacement of L groups by hydrogen reaction. This would be the case for Sn, the element we used in the present study as a control in the vapor generation procedure. In the case of transition and noble metals, the stability of the products is often very low, and the stability of the intermediates depends on the nature of the ligands. The liquid-gas phase transfer step must be fast enough to observe stable products that sequentially include free atoms, metal nanoparticles, colloids, and macroprecipitates (25) (see Figure 7).

Additives can interact with any component of the reacting solution, and their mechanism of action is not clearly established (26). D'Ullivo (8,27) and Xu and Sturgeon (16) considered that DDTC can form complexes with gold or stabilize some borane intermediates. In the case of Ag and Au, nanoparticles were observed in vapor generation reactions (20,28). It can, therefore, be deduced than the use of matrix media modifiers such as surfactants, ligands, or ionic liquids are directly linked to the use of stabilizers (29) in nanoparticle synthesis.

Limits of Detection

Table III lists the limits of detection for the selected Au, Cd, Cu, Ni, Sn, and Zn analytical lines. The limit of detection (LOD) is defined as the element concentration corresponding to 3 times the standard deviation of the reagent blank, which was calculated after analyzing 11 reagent blanks. Similarly, the limit of quantification (LOQ) is the concentration that corresponds to 10 times the standard deviation of the blank.

The increase in the slope obtained in comparison to conventional nebulization does not correspond to a proportional decrease in

the limits of detection. The limits of detection were lower than those obtained using conventional nebulization, except for Cu and Ni. With DDTC, the best limits of detection were obtained for Au (3.6 µg/L) and Cd (0.53 µg/L), whereas for o-phenanthroline the best limits of detection were for Au (3.7 µg/L), Cu (2.5 µg/L), Ni (4.9 µg/L), Sn (1.1 µg/L), and Zn (0.98 µg/L). The limits of detection were similar to other values found in the literature (approximately 1–3 µg/L in mono-elemental detection) (2,13,16,18). The results of this study show an improvement in the detection limits obtained by using 8-hydroxyquinoline for ICP-OES simultaneous determination (Au: 6.1 µg/L, Cd: 8.5 µg/L, Cu: 3.1 µg/L, Sn: 2.5 µg/L, Zn: 1.7 µg/L), except for Ni (9) (3.3 µg/L). The limits of detection listed in the bibliography and using ionic liquids and AFS were higher for Au (6.3 µg/L) and Cu (19 µg/L) (17), but lower for Ni (0.65 µg/L) when combining the modifier with DDTC (19).

Precision

The precision of the methods was estimated by applying the optimized procedure to 11 sample replicates of standards with metal concentrations of 0.15 mg/L for Ag, Au, Cd, Cu, Ni, Zn, and 0.05 mg/L for Sn. The average intensities, standard deviations, and relative standard deviations (RSDs) were calculated. The RSDs obtained for the selected analytical lines are listed in Table III.

The RSDs were higher for o-phenanthroline than for DDTC (using this compound, all RSDs were <5% except for Cd), maybe due to the use of higher reagent flows (2 mL/min vs. 1.5 mL/min) with the same diameter pump tubing. Most of the RSDs were lower than 10% and are good, since they include standard preparation, vapor generation, and detection.

Accuracy

The accuracy of the determination of Cd, Cu, Ni, and Zn was evaluated after the analysis of the wastewater reference material (SPS-WW2 Batch 110, Spectrapure Standards, Oslo, Norway). The determination of the elements was performed using the standard addition method. A 2-mL sample amount was diluted in duplicate to a final volume of 10 mL for the analysis of Cd, Cu, and Zn. In the case of Ni, 0.8 mL of the sample was diluted to 10 mL. Experimental values (mean ± standard deviation; Cd: 90.8 ± 13.9 µg/L with DDTC, 95.1 ± 5.9 µg/L with o-phen.; Cu: 1910 ± 147 µg/L with DDTC, 2010 ± 53 µg/L with o-phen.; Ni: 4997 ± 90 µg/L with DDTC, 4740 ± 55 µg/L with o-phen.; Zn: 3037 ± 163 µg/L with DDTC, 2918 ± 79 µg/L with o-phen.) showed an acceptable agreement with the certified contents of the material (Cd: 100.0 ± 0.5 µg/L, Cu: 2000 ± 10 µg/L, Ni: 5000 ± 25 µg/L, Zn: 3000 ± 15 µg/L).

In the case of Au and Sn, a tap water sample (dilution 5 to 25 mL) was spiked with 0.075, 0.15, 0.3, and 0.45 mg/L of the elements, and the recoveries were calculated, with average values near to 100% (Au: 94.8 ± 6.8 % with DDTC; 100.9 ± 7.0 % with o-phen.; Sn: 99.5 ± 6.5 % with DDTC, 98.8 ± 2.4 % with o-phen.). Therefore, the use of additives in the reaction media for enhancing vapor generation efficiency seems to be an interesting field of research to improve the sensitivity of conventional atomic spectroscopy.

CONCLUSION

An optimization was performed for the simultaneous determination of Au, Cd, Cu, Ni, Zn, and Sn by VG-ICP-OES using o-phenanthroline or DDTC as the reaction media modifier. The limits of detection and precision (RSDs < 10% or

≈ 11% in the case of Cd) were calculated. The limits of detection obtained were lower than those obtained using conventional nebulization, except for Cu and Ni. The use of o-phenanthroline provided better detection limits than DDTC as a whole, and also better than those obtained with 8-hydroxyquinoline in previous studies.

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