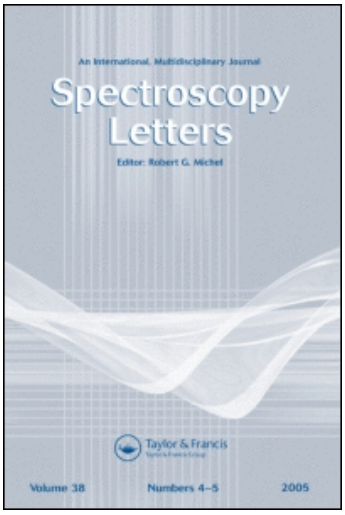

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Method Development for Simultaneous Determination of Transition (Au, Ag, Cd, Cu, Mn, Ni, Pb, Zn) and Noble (Pd, Pt, Rh) Metal Volatile Species by Microwave-Induced Plasma Spectrometry Using Ultrasonic Micronebulizer Dual Capillary Sample Introduction System

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ABSTRACT The commercial ultrasonic nebulizer NOVA-DUO (Optolab, Warsaw, Poland) has been evaluated for the simultaneous determination of transition (Au, Ag, Cd, Cu, Mn, Ni, Pb, Zn) and noble (Pd, Pt, Rh) volatile metal species by microwave induced plasma–optical emission spectrometry (MIP-OES). Simultaneous mixing and nebulization of the two solutions (acidified sample and reductant) on the piezoelectric transducer, with the possibility of flow rate adjustment, permits a wide variation of sensitivity. The vapor-phase species were rapidly transported via a stream of Ar carrier to an MIP–OES for simultaneous multi-element determination. A univariate approach and simplex optimization procedure was used to achieve optimized conditions and derive analytical figures of merit. Analytical performance of the ultrasonic nebulization system was characterized by determination of the limits of detection (LODs) and precision (RSDs) with the ultrasonic nebulizer/dual capillary system (USN/DCS) observed at 15 μL min^{-1} flow rate. An improvement in detection limits was achieved compared with pneumatic nebulization. Detection limits are superior to conventional pneumatic nebulization of elements. The experimental concentration detection limits for simultaneous determination, calculated as the concentration giving a signal equal to three times of standard deviation of the blank (LOD, $3\sigma_{blank}$ criterion, peak height), were 2.49, 1.75, 3.39, 2.13, 4.80, 6.21, 4.26, 2.01, 7.65, 3.92, and 4.65 ng mL^{-1} for Au, Ag, Cd, Cu, Mn, Ni, Pb, Pd, Pt, Rh, and Zn, respectively. The method offers relatively good precision (RSD ranged from 8 to 12%) for liquid analysis and microsampling capability. The accuracy of the method was verified by the

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use of digested certified reference materials (NRCC TORT-1, NIES CRM-13, NIST SRM 2710, INCT SBF-4) and by aqueous standard calibration technique. The measured elements content in reference materials was in satisfactory agreement with the certified values.

KEYWORDS chemical vapor generation, dual-mode sample introduction system, microwave-induced plasma–optical emission spectrometry, transition and noble metals, ultrasonic nebulizer

INTRODUCTION

The chemical vapor generation (CVG) of transition and noble metals was introduced in 1996 by the first report on Cu generation.[1,2] An analyte is simply volatilized upon reduction, most often by borohydride, in a similar fashion to the well-known hydride generation techniques. In principle, the volatilized analyte species can be detected by virtually any method of analytical atomic spectrometry. CVG emerged in recent years as an extension of the classical method of hydride generation (HG), as illustrated by recent review articles.[3–6]

CVG is well known for the convenience of its reaction between tetrahydroborate (III) reductant and target analytes in an acidified sample solution. Recently, the scope of this technique has been expanded to include several transition and noble metals.[7–13] Wickstrøm et al.[7] reported that the matrix (non-hydride forming) elements such as Ni, Co, Cr, and Fe could be transported to the atom cell as an aerosol, formed during hydride generation. Luna et al.[8] described a miniature batch system for the CVG of Ag, Au, Cu, and Zn by tetrahydroborate(III) with a heated quartz tube atomizer and an atomic absorbance spectroscope (AAS) detector. Pohl and Zyrnicki[9] presented evidence for enhanced sample introduction efficiencies for Co, Cr, Fe, and Ni, achieved following reaction of solutions of these metals with tetrahydroborate(III) when using a Meinhard nebulizer. Feng et al.[10] extended the scope of chemical vapor generation for noble and other transition metals. They are tentatively suspected to exist as hydrides. Unreported volatile transition and noble metal species, that is, Mn, Ti, Pt, Ir, Ag, Cd, Au, Co, Cu, Ni, Sn, and Zn have been reported by Duan et al.[11] to be amenable to vapor generation by reaction with tetrahydroborate(III). Pohl and Zyrnicki[12] presented evidence for enhanced sample introduction efficiencies for Au, Pd, and Pt, achieved following reaction of solutions of these metals with tetrahydroborate(III) when using a Meinhard nebulizer. A chemical vapor generation method for simultaneous measurement of Ag, Au, Cd, Cu, Ni, and Zn, using ICP-OES, was developed.[13] Vapor species of Co, Cr, Fe, and Mo were observed as well. The main drawback of the method is the cross-interference of metals when reacting with borohydride.

Ultrasonic nebulizers (USNs) have been shown to be more efficient of aerosol formation and can produce aerosols with smaller and more uniform droplet size. Generating a primary aerosol with a very small mean drop size (ideally $<5\,\mu m$) is an alternative to direct injection to the plasma, because such fine aerosol drops should pass to the plasma with high efficiency. This results in more efficient atomization, higher sensitivity, and reduced matrix effects. It has been reported that ultrasonic nebulizers are capable of operating at flow rates down to $20\,\mu L\ min^{-1}$, without the need for any makeup solvent.[14,15] The ability to provide very high transport efficiency at flow rates in the range of $2–20\,\mu L\ min^{-1}$ suggests good potential for ultrasonic micronebulizers with microwave-induced plasma spectrometry. Ultrasonic nebulizers are popular with inductively coupled plasma (ICP) optical emission (OES) and mass spectrometry (MS). However, over the past decades, only a few ultrasonic nebulizer designs have been developed for use with microwave-induced plasma–optical emission spectrometry (MIP-OES).[16–18] Additional merits of ultrasonic nebulizers for sample introduction in atomic spectrometry have been discussed elsewhere.[19]

The aim of this study was to evaluate, for the first time, the performance of a commercial, specially designed compact continuous microflow ultrasonic nebulizer dual capillary system (μ-USN/DCS) to operate stably with total liquid flows as low as ca. $15\,\mu L\ min^{-1}$ for elemental vapor generation in MIP-OES. Transition elements (Cd, Cu, Mn, Ni, Pb, Zn) and noble metals (Pd, Pt, Rh) are generated *in situ* and analyzed by helium–argon microwave plasma spectrometry. The μ-USN/DCS was made an integrated part of the microwave plasma atomic spectrometer, and the results obtained were shown to be satisfactory.

EXPERIMENTAL

MIP-OES Instrumentation and Operating Conditions

A Carl Zeiss Echelle spectrometer (Model Plasmaquant 100, Jena, Germany) using fiber-optical lightguides and photomultiplier tubes (PMT) and TE_{101} microwave plasma cavity assembly was used and was essentially the same as previously described.[20] Instrument settings, wavelengths, and operational parameters used for the experimental MIP-OES system are summarized in Table 1. These lines were preselected by the producer of the polychromator.

Chemical Vapor Generation Dual Capillary Mode Sample Introduction System

Chemical vapor generation was accomplished in the continuous mode using the commercial ultrasonic nebulizer, model NOVA-DUO (Optolab, Warsaw, Poland),[21] operated in combined conventional ultrasonic nebulization and hydride generation mode (dual mode). In dual mode the acidified solution sample passes through both the nebulizer sample line (capillary) and the hydride generator reductant line (capillary). The volatile vapor species formed are introduced to the microwave plasma by a stream of the nebulizer argon. The water-cooled ultrasonic nebulizer was operated at 1.65 MHz with a forward power of 45 W. The NOVA-DUO system has been described in detail in previous a paper.[22] The experimental conditions are given in Table 2. A schematic diagram of the entire USN/DCS-CVG-MIP-OES system is shown in Fig. 1; Figure 2 shows the main components of the NOVA-DUO, continuous-type USN/DCS system.

The liquid samples were introduced through the ultrasonic nebulizer by means of a Perimax 12 peristaltic pump (Spectec, Erding, Germany). The gas flow rate was controlled by means of a mass flow controller (DHN, Warsaw, Poland) with a pressure regulator. Argon was used as the nebulizing carrier gas and as the plasma gas; helium was used as the plasma gas.

A concentric nebulizer–cyclonic glass spray chamber arrangement was used for comparison purposes.

Gases and Reagents

Compressed, pure argon and helium gases (N-50 purity, 99.999%) obtained from BOC Gazy (Poznań, Poland) were used as plasma gases.

Standard solutions were prepared from a 1000 mg L^{-1} Au, Ag, Cd, Cu, Mn, Ni, Pb, Pd, Pt, Rh,

TABLE 1 Instrumental Parameters for the USN-MIP-OES System

Mounting	Czerny-Turner in tetrahedral setup
Focal length (mm)	500
Spectral range (nm)	193–852
Order lines	28th–123rd
Microwave frequency (MHz)	2450
Microwave power (W)	100–180, variable
Microwave cavity	TE_{101} rectangular, water cooled
Microwave generator	700 W, MPC-01 (Plazmatronika Ltd., Wrocław, Poland)
Plasma viewing mode	Axial
Plasma torch, axial position	Quartz tube, 3.0 mm i.d., air cooled
Argon flow rate (mL min^{-1})	200–1000, variable
Plasma supporting helium flow rate (mL min^{-1})	100–300, variable
Plasma form	Annular
Read	On-peak
Integration time (s)	0.1
Background correction	Fixed point
Determination	Simultaneous
Wavelength (nm) (line type)	Au 242.796 (I), Ag 328.068 (I), Cd 226.502 (II) Cu 324.754 (I), Mn 257.611 (II), Ni 221.647, Pb 405.783 (I), Pd 265.875 (II), Pt 265.944 (I), Rh 343.489 (I), Zn 213.857 (I)

TABLE 2 Chemical Vapor Generation (CVG) and NOVA-DUO Ultrasonic Nebulizer Operating Parameters

Dual capillary ultrasonic nebulization parameters	
Instrument	NOVA-DUO without desolvation system
Solution flow mode	Continuous
Transducer frequency (MHz)	1.65
Acoustic power (W)	45
Transducer type (W)	Piezoelectric quartz plate, water cooled
Spray chamber	Cyclonic
Nebulizer gas (Ar) flow (mL min^{-1})	750
CVG sample introduction	
$NaBH_4$/NaOH solution concentration (% m v^{-1})	1.0/0.1
$NaBH_4$ solution flow rate (μL min^{-1})	15
HNO_3 solution concentration (mol L^{-1})	0.6
Sample solution flow rate (μL min^{-1})	15
Plasma helium flow rate (mL min^{-1})	150
Rinse time between the samples (s)	360

and Zn atomic absorption standards (Titrisol grade, Merck, Darmstadt, Germany). Working standard solutions were freshly prepared daily by diluting appropriate aliquots of the stock solution in 0.6 M HNO_3 prepared from 69% high-purity acid (Merck) in pure water.

Sodium tetrahydroborate (III), used as reducing solution, was prepared daily, by dissolving $NaBH_4$ pellets (Suprapure, Merck, Germany) in high-purity water and stabilizing with 0.1% (m/v) NaOH (Suprapure, Merck, Germany) solution to decrease its rate of decomposition and was used without filtration.

Ultra-high-purity commercial acids (HCl, HNO_3, HF; extra pure, Merck, Darmstadt, Germany) were used to prepare all reagents and samples. Hydrogen peroxide 30% (v/v) was obtained from POCh (Gliwice, Poland). Water was initially deionized (Model DEMIWA 5 ROSA, Watek, Czech Republic) and then doubly distilled in a quartz apparatus (Heraeus Bi18, Hanau, Germany).

Reference Materials

Applicability of the method described in this work was assessed using four reference materials that were chosen to represent liquid and solid sample matrices: NRCC TORT-1 (Lobster Hepatopancreas) supplied by the National Research Council of Canada (NRCC; Ottawa, Canada), NIES CRM-13 (Human Hair) from the NIES (Tsukuba–City, Japan), SRM 2710 (Montana Soil) supplied by the National Institute of Standard and Technology (NIST, Gaithersburg, MD, USA), INCT SBF-4 (Soya Bean Flour) from the Institute of Nuclear Chemistry and Technology (INCT Warsaw, Poland). The certified reference values are available for each of these elements for assessment of the

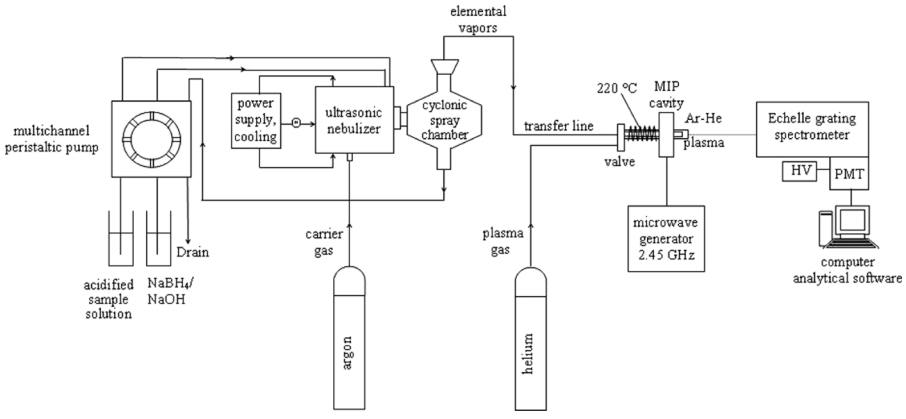


FIGURE 1 Schematic diagram of the elaborated μ-USN/DCS-CVG-MIP-OES system.

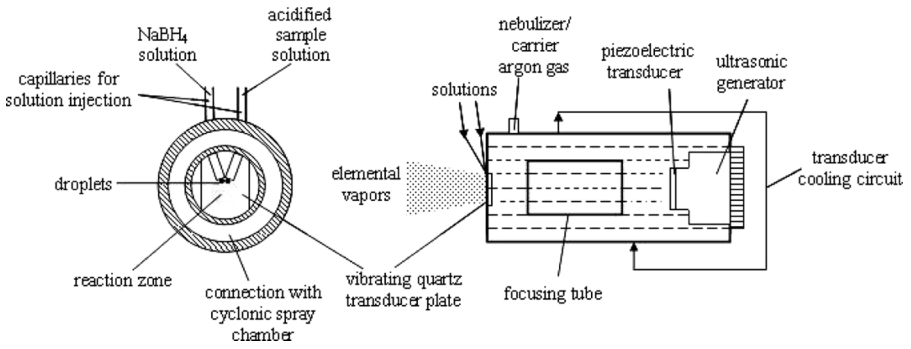


FIGURE 2 **Schematic diagram of the dual capillary elemental vapor generation μ-USN/DCS system.**

method accuracy. All solid reference materials were used as bottled, without further grinding and sieving.

Microwave Digestion System

A laboratory-built prototype of a high pressure–temperature focused microwave heating digestion system, equipped with closed TFM-PTFM (Hostaflon TFM is a chemically modified polytetrafluoroethylene [PTFE]) vessel (30 mL internal volume) based on a design outlined in detail by Matusiewicz[23] was employed for wet-pressure sample digestion.

Analytical Procedures

Microwave-Assisted Sample Digestion at High Pressure in PTFE Vessels

Preparation of all standards and digestion of all samples were conducted under typical laboratory conditions. The microwave-assisted pressurized digestion technique used for biological and environmental samples has been described previously.[23]

Approximately 300 mg of powdered organic reference material (TORT-1, CRM-13, SBF-4) were placed in the 30-mL TFM-PTFE vessel of the microwave digestion system, moistened with 1 mL of 30% H_2O_2, and 3 mL of concentrated HNO_3 was added. The sample was heated for 10 min at 100 W. When working with inorganic materials (SRM 2710), approximately 300 mg of powdered samples was first moistened by 0.5 mL of 30% H_2O_2; then 2 mL of concentrated HNO_3 and 2 mL of 40% HF were used. The samples were heated for 15 min at 150 W. The digested solutions were transferred into 10-mL volumetric calibrated flasks and diluted up to the mark with water. Before further analysis they were appropriately diluted depending upon the concentration level of the elements. In all cases, a corresponding blank was also prepared according to the above microwave-assisted decomposition and dissolution procedures.

Chemical Vapor Generation Procedure

The procedures for elemental vapor generation of samples were accomplished in NOVA-DUO.[21] When manually operated in vapor generation mode, the volatile species were generated continuously and were introduced into the MIP source; the acidified samples and reductant were simultaneously pumped into the ultrasonic nebulizer hydride-generation system to the MIP. In the region of convergence of the two solutions and the carrier argon gas, sample and sodium borohydride aerosol were generated and a reaction occurred to produce the vapors *in situ*. A Perimax12 peristaltic pump (SPETEC, Erding, Germany) was used to feed the nebulizer with the acidic sample solution and sodium borohydride solutions. The waste solution was rapidly removed from the chamber to drains by a peristaltic pump. The NOVA-DUO was rinsed by aspiration acidic water for approximately 10 s after injection of each solution replicate.

MIP-OES Analysis

The plasma was ignited by momentarily inserting an isolated high-purity tantalum wire into the quartz discharge tube and was allowed to warm up for a period of about 15 min prior to analysis. After completion of the generation, the released gaseous products (vapors and hydrogen) produced from liquids by the ultrasonic nebulizer were immediately carried out by the argon plasma carrier gas through the cyclonic spray chamber and into the MIP for excitation in the Ar-He plasma gases. Net analyte emissions were

calculated by taking the simultaneous difference of measured emission intensities on the top of the peak and background near the peak. Instrumental characteristics and operating parameters with the use of the experimental MIP-OES and chemical vapor generation system are listed in Tables 1 and 2. Analytical blanks were also carried through the entire procedure outlined above, to correct for possible contaminants in the reagents used for sample preparation. Quantification of Au, Ag, Cd, Cu, Mn, Ni, Pb, Pd, Pt, Rh, and Zn was made from linear calibration curves. All limits of detection (LODs) given by MIP-OES software were calculated for raw, unsmoothed data based on a 3σ criterion of the background (blank) counts. The LOD, corresponding to a measurement level 3σ above the mean blank intensity, was obtained by using procedural blank solutions.

RESULTS AND DISCUSSION

Dual Ultrasonic Micronebulizer System for Chemical Vapor Generation

The new NOVA-DUO dual system was used to generate the volatile hydrides of Au, Ag, Cd, Cu, Mn, Ni, Pb, Pd, Pt, Rh, and Zn. Operation of the dual system consisted of pumping $NaBH_4$ solution with a peristaltic pump through one capillary and the acidified sample solution was delivered with the same pump through another capillary. Sample and $NaBH_4$ solutions were generated and a reaction occurred *in situ* into the quartz piezoelectric transducer to concurrently produce the volatile species.

In order to test the applicability of the dual system for vapor generation to MIP-OES, an optimization of the Au, Ag, Cd, Cu, Mn, Ni, Pb, Pd, Pt, Rh, and Zn emission signal intensities as a function of the different parameters was carried out.

Optimization of Operating Parameters

The optimization of wavelength was not carried out because the wavelengths used for the determination were preselected by the producer of the polychromator.

Preliminary analytical performance of the Ar/He-MIP was examined by measuring the S/B ratio of selected elements. However, substantial optimization of the gases' parameters for the analytes was not undertaken, because this information was readily available from the literature on excitation and ionization conditions for MIP-OES with pneumatic nebulization[24] (and references cited therein). The comparison of these parameters obtained for mixed plasma with those presented for pure argon plasma and helium plasma with ultrasonic nebulization shows that introduction of helium allowed better detection limits than in pure Ar plasma gas. As a result of the consideration on the above influences, an Ar/He-MIP was selected for all the subsequent experiments, for a plasma gas composition of ca. 80% Ar and 20% He; this is in agreement with results presented earlier.[24]

Simplex Optimization of Operational Variables for Determination of Compromised Optimum

In view of the simultaneous multi-element capability of MIP-OES, the optimum parameters for single determination of all analytes were compared and, in effect, compromise conditions were selected for simultaneous determination (any simultaneous method by definition will use compromise conditions), provided that the chosen value was not totally unsuitable for a particular element. Optimization of all operating conditions simultaneously by simplex procedures was undertaken in these initial investigations. Preliminary experiments were done with HG-MIP-OES of aqueous standard solutions for all elements.

Two different types of experimental variables affect the method. These are as follows: (1) variables controlling the emission response in the microwave plasma; that is, the microwave forward power of the microwave generator; (2) variables such as the argon carrier flow and sample uptake rate that regulate transport; followed by (3) univariate searches for the optimum values of applied power, nebulizing-carrier gas flow rate, and sample uptake rate. A multivariate simplex optimization was used to establish the optimum plasma parameters for low detection limits of selected elements. The optimization was complete in 19 steps, which took approximately 2 hr. The effectiveness of the simplex procedure was confirmed with univariate searches, which

assisted in verifying that the optimum lay near the simplex value.

Microwave Forward Power

The MIP is normally operated at low power levels in the range of 50–150 W. In this work, the stable Ar/He plasma could be maintained at a level of greater than 100 W forward power. Below 100 W power input, no stable discharge was produced. Between 100 and 180 W, neither the intensities of spectral lines nor the S/B ratios showed such a dependence on the power that this would point to a pronounced optimum. In addition, the stability of the background and line signals did not significantly vary with power in the stated range. In general, for all analytical lines of studied elements, S/B ratios usually tend to level off after the microwave power approaching 140 W. The intensities of spectral lines also level but more slowly. As a result of this consideration on the above influences, an optimized power of 160 W was selected as an acceptable value and a practical working range (Table 3 and Fig. 3a).

Carrier Argon and Plasma Helium/Argon Flow Rates

The effect of plasma (support) helium gas flow rate was optimized in our experiments and was selected based upon previous experience and maintaining the plasma stability and plasma shape. Stable operation of the plasma was obtained at gas flow rates of 180 mL min^{-1} (Fig. 3b). It was also observed that the carrier Ar gas stream flow rate has a more significant influence on the emission intensities than the plasma support gas flow rate. The carrier gas affects the formation of the plasma channel (an annular configuration),[25] the residence time of the analyte in the plasma, and the aerosol generation and transport efficiency.[26]

To optimize the carrier (nebulizing) argon gas flow for multi-element determination, the optimum

TABLE 3 **Comparison of Detection Limits (LOD)[a] for Elements Using Ultrasonic (USN-CVG) and Pneumatic Nebulization (PN)**

	USN-CVG			PN			
Element	ng mL^{-1}[b]	pg[c]	RSD (%)	ng mL^{-1}	pg	RSD (%)	X[d]
Au	2.5	37	9	13	198	8	5.3
Ag	1.7	26	9	6.1	92	6	3.5
Cd	3.4	51	12	6.1	91	5	1.8
Cu	2.1	32	9	5.0	75	7	2.4
Mn	4.8	23	10	6.1	92	6	1.3
Ni	6.2	93	11	15	224	6	2.4
Pb	4.3	64	9	13	198	5	3.1
Pd	2.0	30	8	37	558	8	18
Pt	7.6	115	11	201	3015	9	21
Rh	3.9	59	10	74	1118	8	19
Zn	4.6	70	8	11	161	6	2.3

[a]Detection limit defined by three blank criterion (n = 6).
[b]For sample weights of 300 mg.
[c]Sample solution flow rate of 15 μL min^{-1}.
[d]Enhancement (improvement factor).

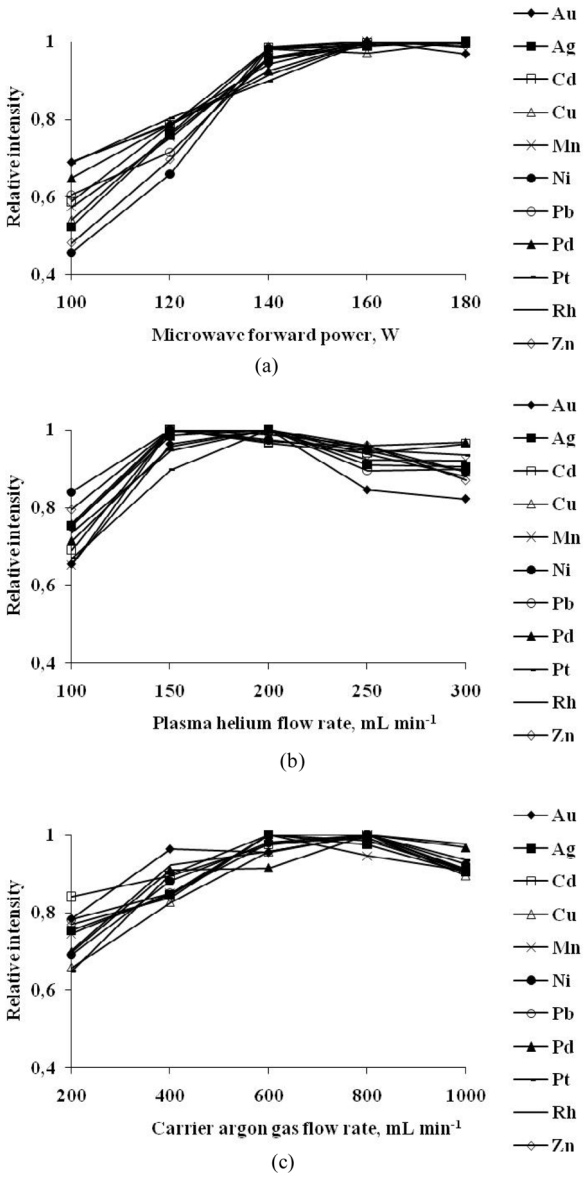
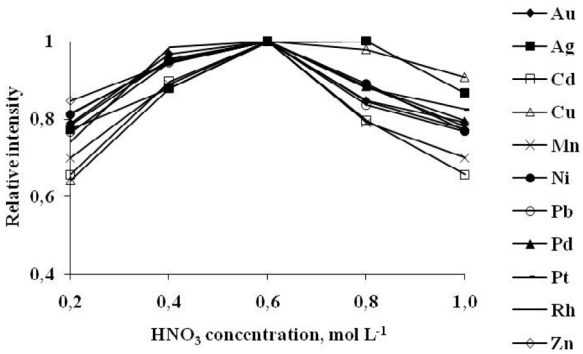
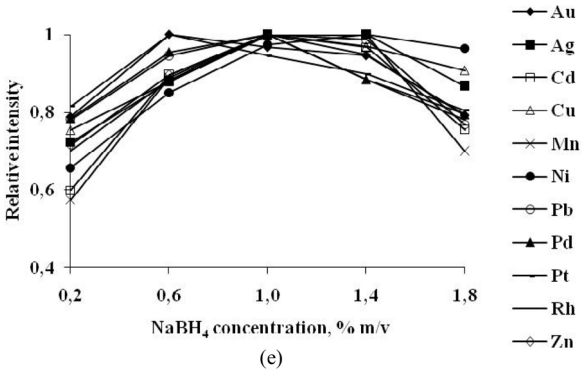


FIGURE 3 **Effect of the variables on the element's normalized emission intensity for NOVA-DUO ultrasonic nebulizer. Influence of (a) microwave forward power; (b) plasma helium flow rate; (c) carrier argon flow rate; (d) HNO_3 concentration; (e) $NaBH_4$ concentration; (f) sample and reductant flow rate on the emission intensity of the elements in the elemental vapor generation technique. The experimental conditions employed are detailed in the Experimental section.**





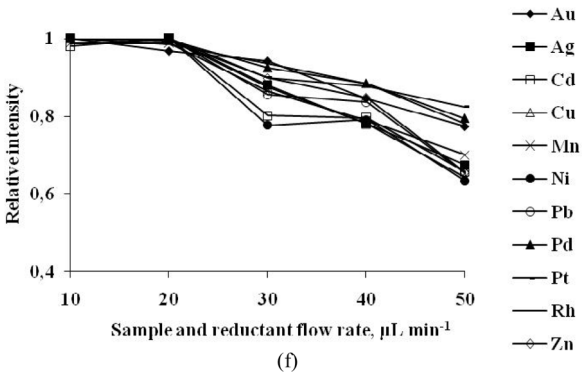


FIGURE 3 CONTINUED.

flow for all elements was estimated in the total range of 200–1000 mL min^{-1} for ultrasonic nebulizer. The effect of carrier argon flow rate on the relative emission intensities is illustrated in Fig. 3c. It was observed that the carrier argon stream flow rate has a significant influence on the emission intensities and thus proved to be a critical parameter. In general, it was observed that when the flow rate was ranged between 200 and 1000 mL min^{-1} for the NOVA-DUO ultrasonic nebulizer, the emission intensities reached maximum at 750 mL min^{-1} for the NOVA-DUO, and with further increase of the flow rate above this value, the emission intensities decreased for all elements. The maxima are the result of opposite effects of nebulizing gas flow on aerosol characteristics and interaction of aerosol with the plasma. Increasing the nebulizing gas flow rate commonly causes a shift of both primary and tertiary drop size distributions to smaller droplet sizes. This in turn leads directly to higher analyte and solvent transport rates. However, these two transport rates exert opposite trends on net signal intensity. In addition, the higher the nebulizing-carrier gas flow, the smaller the residence time of droplets in the plasma. Therefore, the overall effect is shown as a maximum behavior. Therefore, in this study, a 750 mL min^{-1} carrier argon flow rate was chosen for the NOVA-DUO ultrasonic nebulizer.

Chemical Parameters

The effect of hydrochloric acid and nitric acid on net emission intensities of all elements was also investigated. According to the fact that HNO_3 (together with HF) is usually used for sample preparation, this acid was also investigated. For all analytes studied, it was shown that the signal intensity was affected by the nature of the acid, nitric acid. When using HCl the elemental signals were found to be about 10–20% lower than those obtained with HNO_3. Thus, 0.6 mol L^{-1} was chosen for the solution preparation and for the generation of elemental vapors (Fig. 3d).

The generation efficiency greatly depends on whether sodium or potassium tetrahydroborate is used. For this reason, the sodium salt was ultimately preferred because a better generation efficiency and detection limits were obtained. Use of $NaBH_4$ enhanced sensitivity by ca. 10% over KBH_4. Therefore, the concentration of 1.0% $NaBH_4$ stabilized with 0.1% NaOH was adopted and selected for further experiments (Fig. 3e). This appears intuitively correct, because these factors are an integral part of the hydride generation reaction.

Sample and Reductant Flow Rate

The sample uptake rate also proved to be important for this work. To optimize the sample and reductant flow rate for multi-element determinations, first the optimum flow for each individual element was estimated in the range of 10–50 µL min^{-1} (Fig. 3f). It was observed that when the flow rate (sample pumping rate for NOVA-DUO) was low (10–20 µL min^{-1}), the emission leveled off with the

flow rate; however, with the further increase of the flow rate (above 15 μL min^{-1}), the emission intensities would not increase further and began to decrease for all elements. Therefore, in this study a 15 μL min^{-1} (simplex optimization) sample and reductant flow rate was chosen.

Analytical Figures of Merit

A comparison of the detection limits of the present procedure is summarized in Table 3 for conventional pneumatic nebulization (PN) and with ultrasonic nebulization (USN) for MIP-OES.

The analytical performance characteristics were evaluated for each element. The LODs calculated using the IUPAC recommendation (based on a $3\sigma_{blank}$ criterion), determined by six repetitive measurements of the blank involving the entire process and obtained by use of the compromise operating conditions, are summarized in Table 3 and are based on the raw, unsmoothed data. Because no detection limits, for all elements, obtained by identical or similar technique are available, the results are compared to the MIP-OES technique with pneumatic nebulization. From Table 3 it can be seen that the detection limits of the developed procedure are better, compared with PN-MIP-OES. Detection limits obtained for all elements were in the ppb (ng mL^{-1}) range.

The precision of replicate determinations was calculated from the RSD (%) of the mean of five replicate measurements of element standard using a concentration 50-fold above the LOD. Precision was in the range of approximately 9% (evaluated as peak height) and is probably largely determined by the instability of the microwave plasma source. These values can be considered satisfactory, especially due to the large number of parameters governing the performance of the coupled technique. In other words, this reflects the cumulative imprecision of all of the sample solution handling, sample ultrasonic vapor generation, transfer of vapors, excitation, and detection steps.

Validation of the Method by Analysis of Reference Materials

To evaluate the accuracy and precision of the sample introduction system tested on the determination of volatile vapor species (Au, Ag, Cd, Cu, Mn, Ni, Pb, Pd, Pt, Rh, Zn), four certified reference materials were chosen because they were closest in nature to real biological and environmental samples. The results obtained for the analysis of reference materials by ultrasonic nebulization CVG-USN-MIP-OES method using both the external calibration technique and the technique of standard additions are summarized in Table 4. The results obtained by

TABLE 4 Validation of the Method Using Reference Materials[a,b]

	Montana Soil NIST 2710		Lobster Hepatopancreas NRCC TORT-1		Human Hair NIES CRM-13		Soya Bean Flour INCT SBF-4	
Element	Found value	Certified value	Found value	Certified value	Found value	Certified value	Found value	Certified value
Au	1.92 ± 0.18	2[b]	—	—	—	—	—	—
Ag	34.5 ± 2.9	35.3 ± 1.5	—	—	—	—	—	—
Cd	20.1 ± 2.1	21.8 ± 0.2	25.4 ± 2.7	26.3 ± 2.1	0.27 ± 0.04	0.23 ± 0.03	<LOD[d]	0.029[e]
Cu	2875 ± 283	2950 ± 130	446 ± 43	439 ± 22	15.8 ± 1.5	15.3 ± 1.2	14.42 ± 1.41	14.30 ± 0.46
Mn	0.92 ± 0.09%	1.01 ± 0.04%	24.2 ± 2.4	23.4 ± 1.0	3.7 ± 0.4	3.9[d]	33.4 ± 3.4	32.3 ± 1.1
Ni	13.8 ± 1.4	14.3 ± 1.0	2.5 ± 0.3	2.3 ± 0.3	—	—	3.19 ± 3.2	3.12 ± 0.18
Pb	5497 ± 458	5532 ± 80	10.9 ± 1.1	10.4 ± 2.0	5.1 ± 0.5	4.6 ± 0.4	<LOD[d]	0.083[e]
Pd	1.97 ± 0.19	2[b]	—	—	—	—	—	—
Pt	5.09 ± 0.49	5[b]	—	—	—	—	—	—
Rh	4.89 ± 0.47	5[b]	—	—	—	—	—	—
Zn	6896 ± 627	6952 ± 91	171 ± 16	177 ± 10	179 ± 17	172 ± 10	54.6 ± 5.6	52.3 ± 1.3

[a]Results are expressed in μg g^{-1}.
[b]Mean ±standard deviation (n = 3).
[c]Added amount.
[d]Below detection limit.
[e]Information (uncertified) value.

the external calibration technique agree with certified values for all four reference materials, indicating that calibration against an aqueous solution could produce accurate results. All experimental concentrations agreed fairly well with the certified interval element values. Although no interference study was undertaken, it is obvious that there are no systematic errors due to the presence of the matrices. These results clearly also indicate that the sample digestion protocol employed was effective in breaking down organic and inorganic biological and environmental matrices. The precision of replicate determinations was typically around 9% RSD.

CONCLUSIONS

Determination of transition and noble metals as metal vapors in four biological and environmental certified reference materials has demonstrated the viability of this new sample introduction technique. This study has shown that μ-USN/DCS is well suited for sample introduction in such an uncommon plasma spectrochemical source as MIP-OES, in particular where the sample is limited, expensive, or hazardous. Due to the very small sample volume needed for the determination (i.e., $<15\,\mu L$), which is often the case in medical analyses, the method tends itself to sample-limited applications. The technique has the advantage of providing simultaneous multi-element determination of volatile elemental vapors. The elements' vapors are produced *in situ* and analyzed directly by plasma emission spectrometry. The system can be constructed from simple, commercially available equipment.

The use of multivariate optimization is demonstrated in studying the effects and identifying the compromise values of the experimental parameters that are known to influence the vapor generation and spectrometric determination of the elements. However, the application of the multivariate optimization for a single element is more advantageous because it could give the optimum value for the determination of the element in the given technique, without the need to compromise.

Finally, it has to be pointed out that this is the first publication on sample micro-ultrasonic nebulization with elemental vapor generation sample introduction for transition and noble metals determination in microwave-induced plasma spectrometry. Therefore, this article only claims to give a first impression of the power and facilities of a new method of elemental vapors in MIP-OES.

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