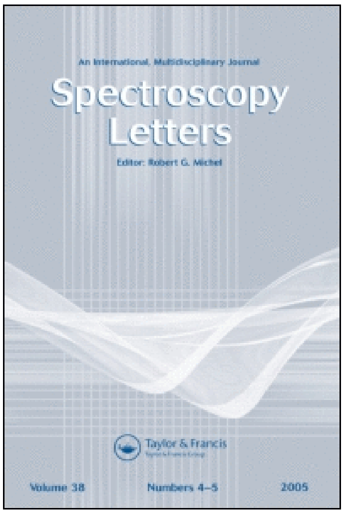

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Analytical Evaluation of an Integrated Ultrasonic Nebulizer-hydride Generator System for Simultaneous Determination of Hydride and Non-hydride Forming Elements by Microwave Induced Plasma Spectrometry

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ABSTRACT The commercial ultrasonic nebulizer NOVA-DUO (ultrasonic nebulizer dual capillary system USN/DCS) has been evaluated for the simultaneous determination of classical hydride forming (As, Bi, Ge, Sb, Se, Sn) and conventional non-hydride forming (Ba, Ca, Fe, Li, Mg, Sr) elements 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 hydrides and aerosols were rapidly transported via a stream of Ar carrier to a MIP for simultaneous multi-element determination by OES. 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 USN/DCS observed at 11 μL min^{-1} flow rate. 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, $3\sigma_{\text{blank}}$ criterion, peak height) were 1.3, 5.9, 6.6, 1.8, 3.6, 2.6, 41, 8.1, 11, 7.5, 9.2, and 12 ng mL^{-1} for As, Bi, Ge, Sb, Se Sn, Ba, Ca, Fe, Li, Mg, and Sr, respectively. The method offers relatively good precision (RSD ranged from 9 to 13%) for liquid analysis and microsampling capability. Interference effects by transition metals have been shown to be corrected by the addition of thiourea, as a pre-reducing agent and masking agent. The accuracy of the method was verified by the use of certified reference materials (NRCC DOLT-2, NRC GBW 07302, NIST SRM 2710, NIST SRM 1643e) and by aqueous standard calibration technique. All results obtained for reference materials were in agreement with certified values at 95% confidence level by Student *t*-test.

KEYWORDS chemical vapor generation, dual-mode sample introduction system, microwave induced plasma optical emission spectrometry, multi-element determination, trace elements, ultrasonic nebulizer

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INTRODUCTION

The introduction of samples by hydride generation and pneumatic nebulization is normally performed separately by using different sample introduction systems. The efficient production of volatile hydride-forming elements results in the significant increase of analyte intensities and improved limits of detection compared to conventional pneumatic nebulization. In environmental laboratories, a large number of elements normally must be determined. This requirement dictates the use of a multi-element technique involving simultaneous determination of hydride and non-hydride forming elements. The disadvantage of conventional hydride generation systems is that only hydride forming elements (As, Bi, Ge, Hg, Pb, Sb, Se, Sn, and Te) can be determined, leaving the other elements to be determined using a conventional sample introduction system. This constraint can be overcome using sample introduction systems that combine conventional nebulization and vapor generation into the same module.

Several multimode sample introduction designs for ICP (-OES, -MS), i.e., introduction of sample aerosols along with gaseous hydrides have been reported in the literature[1–15] that combine nebulization and vapor generation into a single system in order to determine simultaneously both hydride and non-hydride forming elements using hydride generation and conventional aspiration. Wolnik et al.[1] described a tandem nebulization system that allowed simultaneous determination of elements that form volatile hydrides as well as other elements. With this system LODs were improved 6 to 40 times for the volatile hydride-forming elements without decreasing the sensitivity for those that do not form hydrides. Hutton and Preston[2] described a simple modification to the nebulizer assembly that allows either sensitive hydride or conventional solution analysis to be performed with no downtime. Fengzhou et al.[3] developed and integrated a nebulizer-hydride generator system in which the spray chamber for pneumatic nebulization was modified for hydride generation. After modification the spray chamber functioned as a phase separator and generated an aerosol with smaller-diameter droplets. Pohl and Żyrnicki[4] employed a Jobin Yvon hydride generation system (CMA) without a gas-liquid phase separator for the determination of As, Bi, Se, Sn and non-hydride forming elements by the ICP-OES technique. McLaughlin and Brindle[5] reported a multi-mode sample introduction system (MSIS) in which hydride formation takes place at the outlet of the two capillaries, located in a modified cyclonic spray chamber, that transport the sample and sodium borohydride solution. The MSIS system provides convenient means of determining elements, either by nebulization or vapor generation, or simultaneously in the same device. Asfaw and Wibetoe[6–9] applied a commercial MSIS for the determination of elements, introduced as the hydride, simultaneously with the other non-hydride-forming elements. In general, they found that the sensitivity for the hydride-forming elements increased significantly using the dual mode sample introduction compared with pneumatic nebulization. No significant change in sensitivity was observed for the other elements. Zoltan et al.[10] studied a modified cross-flow-type nebulizer coupled with a conventional Scott double-pass spray chamber. In this case, they adapted two introduction channels (for HCl and $NaBH_4$) into the nebulizer in order to introduce the hydride and acid solutions separately. Gómez et al.[11] explored a dual nebulizer sample introduction system for simultaneous determination of volatile element hydrides and other elements. The system consists of two pneumatic nebulizers connected to the conventional spray chamber of the instrument via a simple adaptor. Matusiewicz and Ślachciński[12] used a slurry sampling method for the simultaneous determination of hydride forming (As, Bi, Ge, Sb, Se, Sn) and Hg and non-hydride-forming (Ca, Fe, Mg, Mn, Zn) elements, without total sample digestion using a MSIS system coupled with microwave induced plasma optical emission spectrometry (MIP-OES). They compared the MSIS with the CMA. Wiltsche et al.[13] characterized the commercially available MSIS for simultaneous multielement hydride and non-hydride-forming elements (As, Bi, Co, Cr, Fe, Mn, Mo, Ni, Sb, Se, Sn, Ti, V, W) in high alloy steels and nickel alloys by axial-viewed ICP-OES. Compared with conventional pneumatic nebulization, the LODs for hydride forming elements were enhanced significantly by factors varying from about 2 to 20. Maldonado et al.[14] evaluated the analytical performance of a dual nebulization system for sample nebulization at lower solution uptake rates in ICP-OES, focusing on the operation of two high-efficiency micronebulizers (HEN) coupled to a modified cyclonic spray chamber for the analysis of sub-mL amounts of samples. Benzo et al.[15] described a dual sample introduction system that combines the benefits of nebulization and vapor generation in a single device. It consists of two commercial conventional concentric nebulizers coupled to a modified cyclonic chamber. Finally, in 1989, a continuous-type 3 MHz ultrasonic nebulizer dual capillary system was developed for flame AAS.[16] Simultaneous mixing and nebulization of the two solutions on the piezoelectric transducer, with the possibility of flow rate adjustment, permits a wide variation of sensitivity which was an essential advantage over the described pneumatic nebulizer dual capillary system.[16] To our knowledge, no paper(s) have been published for the simultaneous determination of hydride and non-hydride-forming elements, using solution sampling chemical vapor generation/ultrasonic nebulization microwave induced plasma-optical emission spectrometry with dual-mode sample introduction system.

In our previous experiments[12] we described the simultaneous determination of several important hydride-forming and non-hydride-forming elements in reference materials using a MSIS system and an axially viewed MIP coupled to an Echelle spectrometer. In the present study we characterized ultrasonic nebulizer-hydride generator system (NOVA-DUO) for simultaneous multi-element determination of low ppb hydride and non-hydride-forming elements in certified reference materials using the NOVA-DUO coupled to MIP-OES.

In this paper we will describe, for the first time, the development of a simultaneous multi-element ultrasonic nebulizer dual capillary USN/DCS-HG/NEB-MIP-OES method (by using a continuous micro-flow mode system) for the quantitative determination of As, Bi, Ge, Sb, Se, Sn, and Ba, Ca, Fe, Li, Mg, Sr in certified reference materials, using a dual-mode sample introduction system. It also describes the MIP-OES instrumental operating parameters, as well as the simultaneous HG and NEB experimental parameters and an evaluation of the main analytical figures of merit.

EXPERIMENTAL

MIP-OES Instrumentation and Operating Conditions

A Carl Zeiss Echelle spectrometer (Model PLASMAQUANT 100) using fibre-optical light-guides and photomultiplier tubes (PMT) and TE_{101} microwave plasma cavity assembly was used, and was essentially the same as previously described.[17] Instrument settings, wavelengths, and operational parameters used for the experimental MIP-OES system are summarized in Table 1. These lines were pre-selected by the producer of the polychromator.

Hydride Generation and Liquid Nebulization Dual Capillary Mode System

Chemical vapor generation and liquid nebulization was accomplished in the continuous mode using the commercial ultrasonic nebulizer, model NOVA-DUO (OPTOLAB, Warsaw, Poland),[18] operated in combined conventional ultrasonic nebulization and hydride generation mode (dual-mode).

TABLE 1 **Plasma Operating Conditions for Ar/He-MIP-OES Studies**

Microwave frequency/MHz	2450
Microwave cavity	TE_{101} rectangular, water cooled
Microwave power/W	160
Plasma torch	Quartz tube, 3.0 mm i.d., air cooled
Plasma viewing mode	Axial
Integration time/s	0.1
Determination	Simultaneous
Wavelengths/nm (line type)	As 228.811 (I); Bi 223.061 (I) Ge 303.907 (I); Sb 217.581 (I); Se 196.085 (I); Sn 242.949 (I); Ba 455.403 (II); Ca 393.366 (II); Fe 238.204 (II); Li 670.776 (I); Mg 285.213 (I); Sr 407.771 (II)

TABLE 2 Instrumental Parameters Used for Hydride Generation and Nebulization Studies

Dual capillary ultrasonic nebulization parameters	
Instrument	NOVA-2 without desolvation system
Solution flow mode	Continuous
Transducer frequency/MHz	1.65
Acustic power/W	45
Transducer type/W	Piezo-electric quartz plate, water cooled
Spray chamber	Cyclonic
Nebulizer gas (Ar) flow rate/mL min^{-1}	500
Hydride generation/nebulization	
$NaBH_4$/NaOH solution concentration/% m v^{-1}	0.6/0.1
$NaBH_4$ solution flow rate/μL min^{-1}	11
HNO_3 solution concentration/mol L^{-1}	1.2
Sample solution flow rate/μL min^{-1}	11
Tiourea solution concentration/mol L^{-1}	1.0
Pre-reduction time/min	40
Carrier argon flow rate/mL min^{-1}	500
Plasma helium flow rate/mL min^{-1}	180
Rinse time between the samples/s	360

In dual-mode the acidified solution sample passes through both the nebulizer sample line (capillary) and the hydride generator reductant line (capillary). The hydrides formed are introduced to the microwave plasma simultaneously with the sample aerosol by stream of the nebulizer argon. The quartz tube (plasma torch) was heated by means of a heating tape wound around it. 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 a previous paper;[19] and will not be discussed again here. The experimental conditions are given in Table 2. A schematic diagram of the entire USN/DCS-HG/NEB-MIP-OES system is shown in Figs. 1 and 2 shows the main components of the NOVA-DUO, continuous type USN/DCS.

The liquid samples and reductant were introduced through the ultrasonic nebulizer by means of a Perimax12 peristaltic pump (SPETEC, 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. The flow rate of Ar introduced through the inlet was maintained by an external mass flow controller.

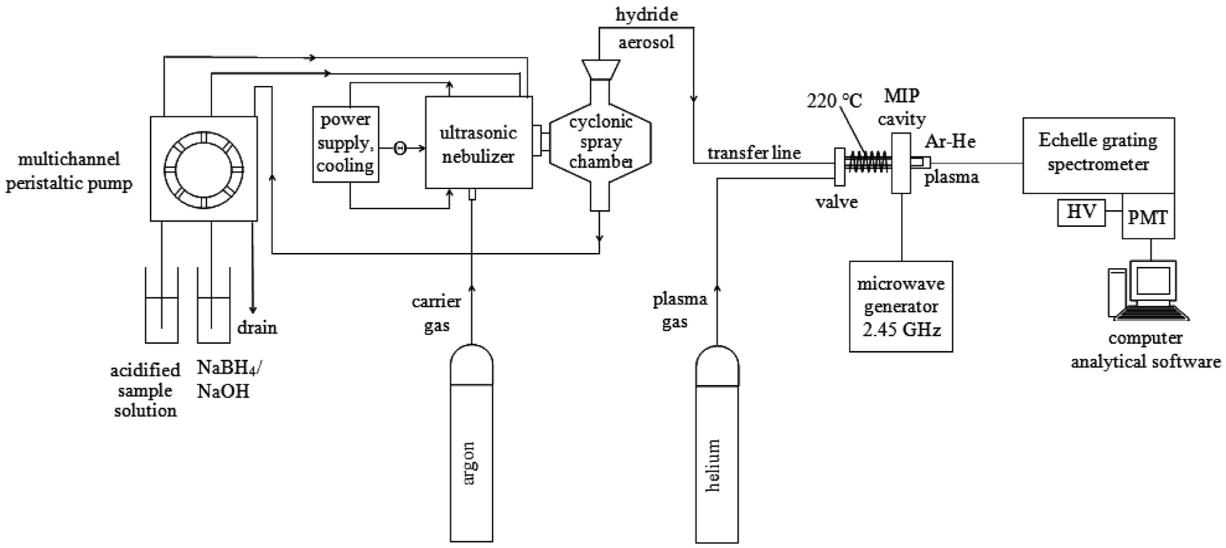


FIGURE 1 Schematic diagram of the elaborated μ-USN/DCS-HG/NEB-MIP-OES system.

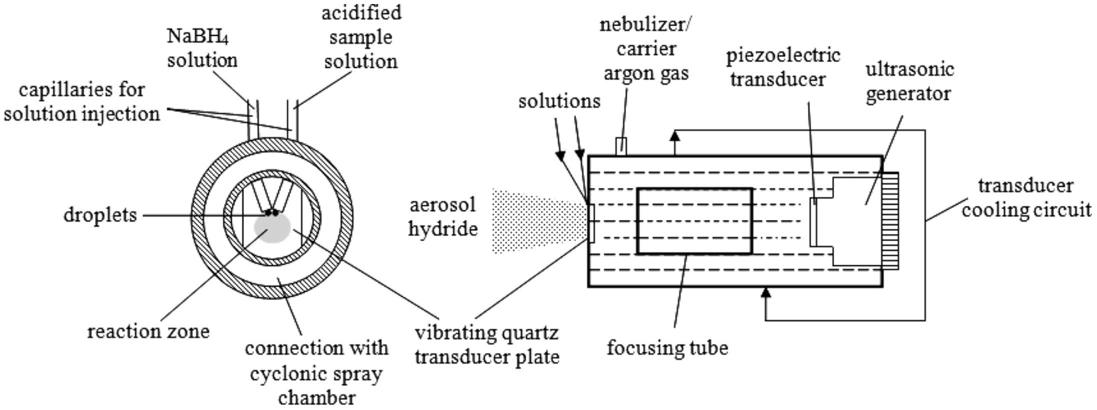


FIGURE 2 Schematic diagram of the dual capillary µ-USN/DCS-HG/NEB system.

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 $1000\,\mathrm{mg\,L^{-1}}$ As, Bi, Ge, Sb, Se, Sn, Ba, Ca, Fe, Li, Mg, and Sr atomic absorption standards (Titrisol grade, Merck, Darmstadt, Germany). Working standard solutions were freshly prepared daily by diluting appropriate aliquots of the stock solution in 1.5M 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.

Thiourea was prepared by dissolving the powder (Fluka, Buchs, Switzerland) in water to yield a 1M solution.

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 which were chosen to represent liquid and solid sample matrices: NRCC DOLT-2 (Dogfish Liver) supplied by the National Research Council of Canada (NRCC, Ottawa, Canada), CRM GBW 07302 (Stream Sediment) from the National Research Center for CRMs (China), SRM 2710 (Montana Soil) and SRM 1643e (Trace Elements in Water) supplied by NIST (USA). The certified reference values are available for each of these elements for assessment of the 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 PTFE) vessel (30 mL internal volume) based on a design outlined in detail by Matusiewicz[20] was employed for wet-pressure sample digestion.

ANALYTICAL PROCEDURES

Microwave-Assisted Sample Digestion at High Pressure in TFM-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.[20]

Approximately 300 mg of powdered organic reference material (DOLT-2) 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 (GBW 07302, Soil 2710), approximately 300 mg of powdered samples were 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 a 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.

Simultaneous Hydride Generation and Conventional Nebulization Procedure

The procedures for hydride generation of liquid samples and liquid nebulization of samples were accomplished in NOVA-DUO.[18] When manually operated in combined conventional nebulization and vapor generation mode (dual-mode), the hydrides were generated continuously and were introduced into the MIP source; the acidified samples 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 *in situ* the hydride and aerosol. A Perimax12 peristaltic pump 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 peristaltic pump. The NOVA-DUO was rinsed by aspiration acidic water for approximately 10 s after injection of each solution replicate.

Simplex Optimization Procedure

A simplex optimization approach was undertaken to establish the best conditions for liquid nebulization, transport and excitation. The parameters optimized are listed in Table 2.

Simplex optimization experiments were performed using a software package (Multisimplex AB, Karlskrona, Sweden). The optimization was carried out on ultrasonic nebulizer in order to establish the "real" experimental conditions. Cyclonic spray chamber was used on all these experiments. Net signal-to-background ratio (S/B) was taken as the criterion of merit. Some preliminary univariate experiments (searches) were performed prior to the simplex optimization in order to establish the boundaries values of each parameter. Three measurements for each variable were conducted at the value of interest. Between each experiment, a blank corrective experiment was run to ensure stable and repeatable results.

The optimum conditions obtained from this procedure were then used to run standard element solutions and quantify the elements present in the dissolved samples.

USN/DCS-HG/NEB-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 and nebulization, the released gaseous products (hydrides and hydrogen) and aerosols produced from liquids by the ultrasonic nebulizer, were immediately carried out by the argon plasma carrier gas through the cyclonic spray chamber (the chamber was directly connected with the plasma torch) 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 hydride generation and nebulization 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 As, Bi, Ge, Sb, Se, Sn, Ba, Ca, Fe, Li, Mg, and Sr was made from linear calibration curves. All limits of detection (LOD) 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 Hydride Generation and Liquid Nebulization

The new NOVA-DUO dual capillarysystem was used to generate the volatile hydrides of As, Bi, Ge, Sb, Se, Sn and liquid nebulization of Ba, Ca, Fe, Li, Mg, and Sr. Operation of the dual system consisted of pumping $NaBH_4/NaOH$ 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 continuously and a reaction occurred *in situ* into the quartz piezoelectric transducer to concurrently produce the volatile hydrides and were introduced into the MIP source; the liquid solution was introduced via another capillary to the quartz piezoelectric transducer and aerosols were introduced into the MIP. A SPETEC peristaltic pump was used to feed ultrasonic nebulizer with the acidic sample solution and sodium borohydride solutions. The waste sample solution was rapidly removed from the cyclonic spray chamber, working as a gas-liquid phase separator, to drains by peristaltic pump. The NOVA-DUO was rinsed by aspiration acidic water for approximately 30 s after injection of each sample replicate.

In order to test the applicability of the dual system for hydride generation and ultrasonic nebulization to MIP-OES, an optimization of the As, Bi, Ge, Sb, Se, Sn and Ba, Ca, Fe, Li, Mg, Sr emission signal intensities as a function of the different parameters was carried out.

Optimization of Operating Parameters

In view of the simultaneous multielement 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 USN/DCS-HG/NEB-MIP-OES of aqueous standard solutions for all elements.

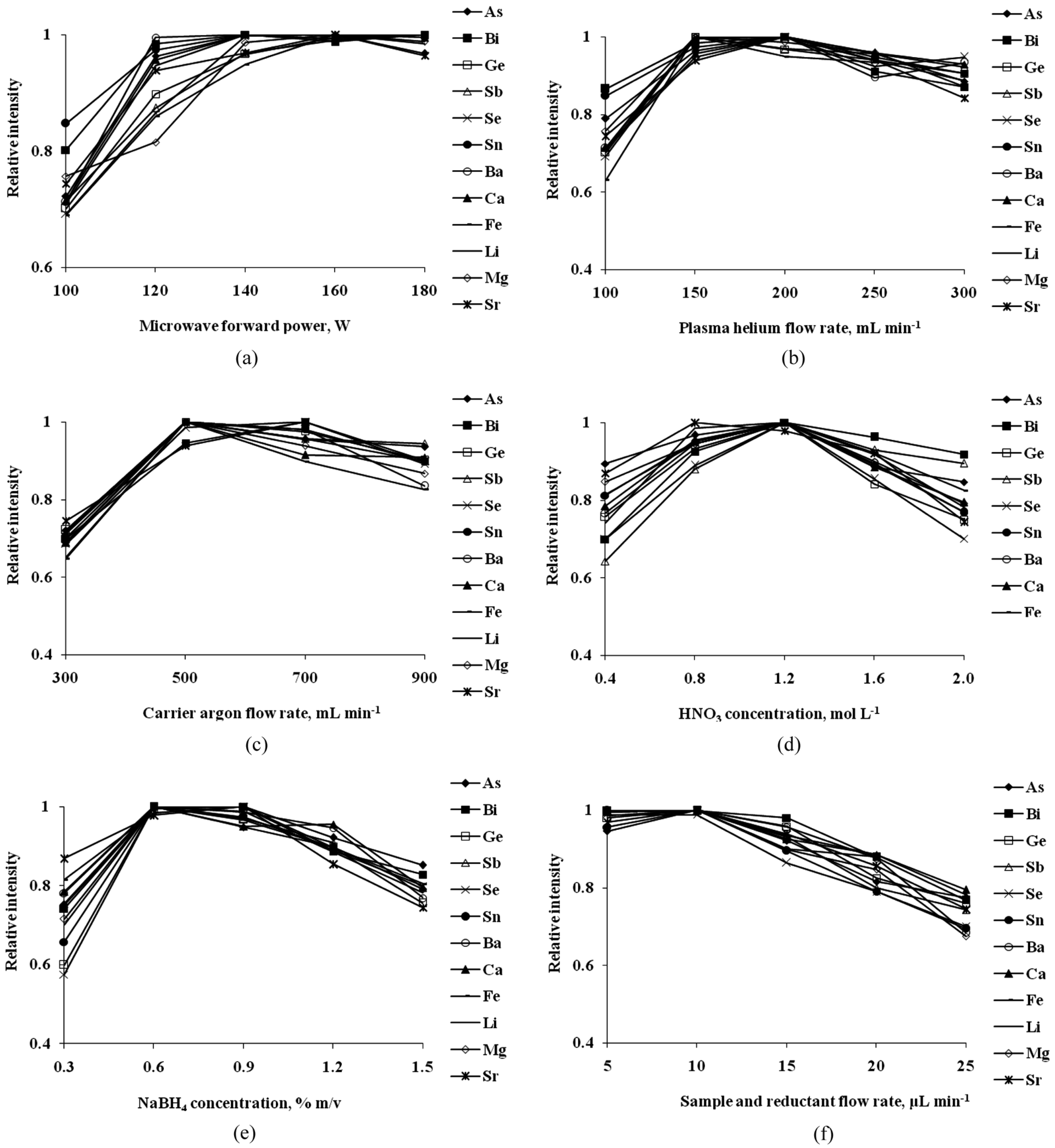
Two different types of experimental variables affect the method. These are as follows: first, variables controlling the emission response in the microwave plasma, that is, the microwave forward power of the microwave generator. Second, variables such as the argon carrier flow and sample uptake rate that regulate transport. Followed by 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 h. The effectiveness of the Simplex procedure was confirmed with univariate searches, which assisted in verifying that the optimum lay near the simplex value.

The optimization of wavelength was not carried out because the wavelengths used for the determination were pre-selected 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, as this information was readily available from the literature on excitation and ionization conditions for MIP-OES with pneumatic nebulization[21] (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 to achieve 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 approximately 80% Ar and 20% He; this is in agreement with results presented earlier.[21]

Establishment of MIP-OES Operating Conditions

The MIP is normally operated at low power levels in the range of 50 to 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 200 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 2 and Fig. 3a).



(a)

(b)

(c)

(d)

(e)

(f)

FIGURE 3 Effect of the variables on the element's normalized emission intensity for NOVA-2 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 hydride generation and sample nebulization technique. The experimental conditions employed are detailed in the Experimental.

Selection of Hydride Generation Conditions

The effect of hydrochloric acid and nitric acid on net emission intensities of all elements was also investigated. It was shown for all analytes studied, the signal intensity was affected by the nature of the acid, nitric acid. Thus, a 1.2 mol L^{-1} was chosen for the solution preparation and for the generation of volatile species (hydride vapors) and liquid nebulization (aerosols) (Fig. 3d).

The rate of generation of volatile vapors greatly depends on the concentration of $NaBH_4$ and acidity. The concentration of 1.0% $NaBH_4$ stabilized with 0.1% NaOH was adopted (Fig. 3e). This appears intuitively correct, since these factors are an integral part of the hydride generation reaction.

On the other hand, a pre-reduction step is needed to overcome possible errors in total analyte hydride determination. In the present work, the thiourea was used as an efficient reductant/masking agent for hydride generation in the presence of a high concentration of transition metals. A concentration of 1.0 mol L^{-1} of thiourea and a contact time of 40 min were selected as convenient for the pre-reduction of all element species.[19] In this case, the introduction of a reductant or masking agent like thiourea is recommended in order to avoid any loss of sensitivity during hydride generation.

The sample uptake rate also proved to be important for this work. To optimize the sample and reductant flow rate for multielement determinations, first the optimum flow for each individual element was estimated in the range of 5 to 25 μL min^{-1}(Fig. 3f). It was observed that when the flow rate (sample pumping rate for NOVA-DUO) was low (5 to 10 μL min^{-1}), the emission intensities increased with the flow rate; when the flow rate went up to approximately 10 μL min^{-1}, the emission intensities reached maximum; however, with the further increase of the flow rate (above 10 μL min^{-1}), the emission intensities would not increase further and began to decrease for all elements. Therefore, in this study a 11 μL min^{-1} (Simplex optimization) sample and reductant flow rate was chosen.

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} (Table 3 and 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),[22] the residence time of the analyte in the plasma, and the aerosol generation and transport efficiency.[23]

To optimize the carrier (nebulizing) argon gas flow for multi-element determination, the optimum flow for all elements was estimated in the total range of 300 to 900 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 300 to 900 mL min^{-1} for NOVA-DUO nebulizer, the emission intensities reached maximum at 500 mL min^{-1} for NOVA-DUO, and with further

TABLE 3 **Analytical Figures of Merit**

Parameter	As	Bi	Ge	Sb	Se	Sn	Ba	Ca	Fe	Li	Mg	Sr
Analysis wavelength/nm	228.811	223.811	303.907	217.582	196.026	242.949	455.403	393.366	238.204	670.776	285.213	407.771
Detection limit[a] (3σ)/ng mL^{-1}	1.3	5.9	6.6	1.8	3.6	2.6	41	8.1	11	7.5	9.2	12
Detection limit[a] (3σ)/ng g^{-1}	42	195	221	61	121	87	1367	269	367	250	307	400
Absolute detection limit[b]/pg	14	65	73	20	40	29	451	89	121	83	101	132
Precision/% RSD	9	11	10	11	13	10	12	11	13	10	10	9

[a] For sample weights of 300 mg.

[b] Sample solution flow rate of 11 μL min^{-1}.

TABLE 4 **Validation of the Method Using Reference Materials. Results are Expressed in μg g^{-1}**

	Montana soil NIST 2710		Stream sediment NRC GBW 07302		Dogfish liver NRCC DOLT-2		Water NIST 1643e	
Element	Found value	Certified value	Found value	Certified value	Found value	Certified value	Found value	Certified value
As	108 ± 10	105 ± 8	6.0 ± 0.6	6.2 ± 1.8	16.3 ± 1.7	16.6 ± 1.1	55.47 ± 6.04	58.98 ± 0.70
Bi	–[a]	–	1.67 ± 0.17	1.64 ± 0.34	–	–	12.88 ± 1.38	13.75 ± 0.15
Ge	–	–	1.69 ± 0.18	1.70 ± 0.82	–	–	2.89 ± 0.29	3.0[b]
Sb	19.2 ± 1.9	19.4 ± 1.8	0.42 ± 0.05	0.46 ± 0.34	–	–	56.90 ± 5.71	56.88 ± 0.60
Se	1.54 ± 0.15	1.52 ± 0.14	–	–	5.95 ± 0.61	6.06 ± 0.49	12.09 ± 1.13	11.68 ± 0.13
Sn	–	–	28 ± 3	29 ± 8	–	–	2.79 ± 0.29	3.0[b]
Ba	718 ± 73	707 ± 51	196 ± 20	185 ± 74	–	–	528.2 ± 5.4	531.0 ± 5.6
Ca	1.21 ± 0.12%	1.25 ± 0.03%	–	–	–	–	3.19 ± 0.21%	3.15 ± 0.11%
Fe	3.27 ± 0.34%	3.38 ± 0.10%	–	–	1069 ± 110	1103 ± 47	99.2 ± 10.1	95.7 ± 1.4
Li	–	–	95 ± 10	101 ± 12	–	–	17.9 ± 1.8	17.0 ± 1.7
Mg	0.840 ± 0.082%	0.853 ± 0.042%	–	–	–	–	0.86 ± 0.09%	0.78 ± 0.01%
Sr	247 ± 25	240[c]	–	28 ± 22	–	–	320.7 ± 3.4	315.2 ± 3.5

[a] Not determined.

[b] Added amount.

[c] Information(uncertified) value.

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 500 mL min^{-1} carrier argon flow rate was chosen for NOVA-DUO ultrasonic nebulizer.

ANALYTICAL FIGURES OF MERIT

The analytical performance characteristics were evaluated for each element. The limit of detection (LOD) calculated using the IUPAC recommendation (based on a $3\sigma_{\text{blank}}$ criterion), determined by 10 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. 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 10% (evaluated as peak height) and is probably largely determined by the instability of the microwave plasma source. These values can be considered satisfactory, especially owing 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 hydride generation and nebulization, transfer of vapors and aerosols, 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 hydrides (As, Bi, Ge, Sb, Se, Sn) and non-hydride elements (Ba, Ca, Fe, Li, Mg, Sr), 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 USN/DCS-HG/NEB-MIP-OES method using both the external calibration technique and the technique of standard additions, are summarized in Table 4. The results obtained by 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

The NOVA-DUO ultrasonic nebulizer system applied in this work has potential benefits in MIP-OES for the simultaneous determination of some classical hydride forming elements (As, Bi, Ge, Sb, Se, Sn) and conventional elements (Ba, Ca, Fe, Li, Mg, Sr) in the certified reference materials using solution sampling (USN/DCS-HG/NEB-MIP-OES). Due to the very small sample volume needed for the determination (≈10 μL), 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 hydride forming and non-hydride forming elements. The elements' hydrides and non-hydrides are produced *in situ* and determined directly by plasma emission spectrometry.

The use of multivariate optimization is demonstrated in studying the effects and identifying the compromise values of the experimental parameters which are known to influence the hydride generation and nebulization and spectrometric determination of the elements.

Finally, it has to be pointed out that this is the first publication on the sample micro ultrasonic nebulization with hydride generation and solution nebulization sample introduction for elemental determination in microwave induced plasma spectrometry. Therefore, this paper only claims to give a first impression of the power and facilities of a new method of elementals MIP-OES and/or mass spectrometry.

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