

Continuous hydride generation in the presence of L-cysteine
for the determination of arsenic, bismuth, antimony and tin in steels
by inductively coupled plasma atomic emission spectrometry

by

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A thesis

Presented to the Department of Chemistry
in partial fulfillment of the requirements
for the degree of
Master of Science

July 1998

Brock University

St. Catharines, Ontario

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Abstract

Arsenic, bismuth, germanium, antimony and tin were simultaneously determined by continuous hydride generation and inductively coupled plasma-atomic emission spectrometry.

Hydrides were introduced into four different types of gas-liquid separators. Two of the gas-liquid separators were available in-house. A third was developed for this project and a fourth was based on a design used by CETAC. The best signal intensity was achieved by the type II frit-based gas-liquid separator, but the modified Cetac design gave promise for the future, due to low relative standard deviation.

A method was developed for the determination of arsenic, bismuth, antimony and tin in low-alloy steels. Four standard reference materials from NIST were dissolved in 10 mL aqua regia without heat. Good agreement was obtained between experimental values and certified values for arsenic, bismuth, antimony and tin. The method was developed to provide the analyst with the opportunity to determine the analytes by using simple aqueous standards to prepare calibration lines. Within the limits of the samples analyzed, the method developed is independent of matrix.

Acknowledgements

I would like to thank Professor Ian D. Brindle for his guidance, enthusiasm during the course of my studies, encouragement and correction of my English throughout this work.

Thank you also to my committee Professor J.M. Miller and Professor J.S. Hartman for their help throughout this thesis.

I am grateful to Canadian International Development Agency (CIDA) for the scholarship and Burapha University, Thailand for the opportunity to further my studies.

I would also thank all staff, faculty members and my friends in Chemistry Department and Technical Services of Brock University for their help during two years at Brock University.

Thank you to Perkin Elmer for the used of the Optima 3300 DV ICP-AES during this thesis.

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Introduction

- **Hydride generation**

Hydride generation is an efficient sample introduction method for the determination of elements in Group IV-A, V-A and VI-A. In the past, signals from elements such as arsenic, antimony, bismuth, germanium, lead, selenium, tellurium and tin were insufficient to enable direct quantitative determination at trace level by conventional aspiration or nebulization via a pneumatic nebulizer. In 1969, Holak (1) utilized the generation of arsine, used in the Marsh reaction and Gutzeit method, for the determination of arsenic. He collected the arsine in a liquid nitrogen trap which was then warmed and passed into the air acetylene flame of atomic absorption spectrometer with a stream of nitrogen. By separating the arsine from the sample solution, interferences from the sample matrix are eliminated. The success of his method was further extended to the determination of other hydride forming elements (2-5). Fernandez (2) collected hydrides in a balloon reservoir and subsequently introduced them into an argon hydrogen-entrained air flame for the determination of arsenic, antimony, bismuth, selenium, tellurium, germanium and tin after reduction with sodium borohydride. Later, Fleming and Ide (3) determined arsenic, antimony, bismuth, lead, selenium, tellurium and tin in steels by hydride generation atomic absorption spectrometry. The detection limits in steel of 1 ppm for arsenic, antimony, bismuth, selenium and tellurium, 2 ppm for tin and 7 ppm for lead are reported. The volatile hydrides of these elements are easily generated and readily separated from the solution in high yield at ambient temperature. The efficiency of hydride generation is dependent upon the experimental conditions and particularly the oxidation state of the analytes. These volatile hydrides are arsine (AsH_3), stibine (SbH_3), bismuthine (BiH_3), germane (GeH_4), plumbane (PbH_4), hydrogen selenide (H_2Se), hydrogen telluride (H_2Te) and stannane (SnH_4).

There are four steps in the hydride generation technique. The first step is adjustment of the oxidation state. This state is most important for some elements, such as arsenic, antimony, selenium and tellurium, which commonly exist in two oxidation states. Sodium borohydride is not efficient for the reduction of these elements in high oxidation states, so prereduction is necessary (6-10). The second step is generation and volatilization of hydrides. In this step, the acidified sample reacts with reducing agent and volatile hydrides are released from the sample solution. The third step is collection and transfer of hydrides in which the purge gas (e.g. argon or nitrogen) transports the volatile hydrides into the flame or plasma. The final step is atomization of hydride in the detection system. Hydrides are decomposed to metal atoms and subsequently measured by an appropriate detection system such as atomic absorption, atomic emission or atomic fluorescence spectrometry.

- **Advantages and disadvantages of hydride generation**

The main advantage of hydride generation technique is that the elements of interest can be separated from almost all other accompanying materials. Only a few elements can form gaseous compounds with borohydride under the experimental conditions. Spectral interferences, such as background attenuation by matrix elements and chemical interferences, encountered in the detection system, are essentially eliminated. The analyte is simultaneously concentrated and a great portion of homogeneous analyte can be delivered to the spectrometer for determination. The transport efficiency of volatile hydrides approaches 100% and thus sensitivity and detection limit are improved. Through the hydride generation process, the sensitivity is improved by 10-1,000 fold over nebulization procedures, depending on the elements and analytical conditions (11-15). The hydride generation system is simple, easy to connect with the spectrometric system and allows a rapid switchover from hydride to normal liquid sample introduction. Moreover, it can be easily automated for routine analysis.

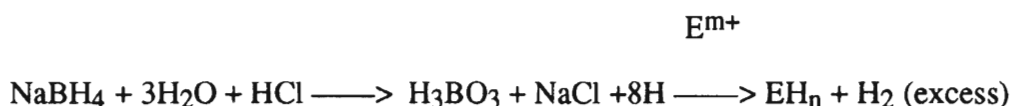
However, hydride generation is not a trouble-free method. The disadvantages of the approach are also well-recognized. For solid samples, the success of the method depends on the dissolution process that is appropriate to the elements of interest. The method still needs a relatively large sample and significant reagent consumption. The reducing solution (sodium borohydride) should be prepared fresh daily. In the presence of some matrices, such as copper, cobalt, nickel, iron, palladium and platinum, which can be reduced easily by sodium borohydride, the efficiency of the reduction during the hydride formation in liquid phase can be reduced. The reduction may be caused by changes in hydride generation rate or because a decreased fraction of the hydrides is released from the sample solution (16-22). Under such circumstances, the concentration of sodium borohydride solution has been increased (17). In contrast, it has been argued that this assumption might be wrong for some experimental conditions (22-24). In addition, the pH of the solution can be critical for some hydride forming elements. Moreover, in order to determine the total concentration, the oxidation state of the analyte should be considered because errors can arise if the oxidation states of the analyte in the sample and standard are different (25, 26). So, in some cases, a prereduction step is required before hydride generation. In the gas phase, mutual effects between the hydride forming elements must be considered (27-30). Patrick and Krivan (29) reported that the interference of bismuth and tellurium on antimony, arsenic, selenium and tin tend to occur in the hydride generation stage.

- **Hydride generation reactions**

The reduction reaction of hydride forming elements to their hydrides can be done by several reducing agents. Earlier studies used metal-acid reaction to produce hydrides. They used zinc-hydrochloric acid (31-33) or a combination of SnCl_2 and KI as a reducing agent (1, 33-41), but those reactions are slow. In most cases, it is necessary to trap the hydride before introduce to determine by spectrometry. Some used the mixture of $\text{Mg-TiCl}_3\text{-HCl}$

(42, 43). However, the metal-acid reaction still has limited application, due to its limitation for multielement analysis and it is time consuming.

The most popular and effective method for multielement analysis uses sodium borohydride solution as a reducing agent. Sodium borohydride reacts rapidly in the presence of acid and a high yield can be achieved. The reaction is shown in the following equation :



where E is the analyte element and m may or may not be equal to n.

Nakahara (25) reviewed papers on hydride generation. He reported that the concentration of NaBH₄ varies from system to system, ranging from 0.1-10 %. The NaBH₄ solution needs to be stabilized by alkalization with NaOH or KOH. Concentrations of 0.1-2 % NaOH or KOH are appropriate to stabilize the NaBH₄ solutions. Even so NaBH₄ solutions are relatively unstable and should be prepared daily. Knechel and Fraser (44) suggest the filtration of NaBH₄ solution through 0.45 µm membrane filter, but later papers suggest that it is not necessary.

Type of acid and concentration are the important factors for hydride generation by borohydride-acid reaction. Type of acid and concentration depend on the element of interest. Most workers used hydrochloric acid for their hydride generation system (6, 10, 45-51). Several workers use nitric acid (9, 10, 50, 51), due to its use in the dissolution of most samples of metals. Nakahara (49) reported that for the determination of tin, nitric acid gave higher signal than hydrochloric acid. Sulfuric acid is also used in combination with hydrochloric acid (4-5). Organic acids, such as tartaric acid, malic acid and oxalic acid have been used for generation of hydrides, but signal intensities are lower than those where inorganic acids are used (50). For the determination of germanium, organic acids seem to be successful. At high acid concentration, hydrogen production is increased and results in the dilution effect. In some systems it can extinguish the plasma.

- **Hydride generation system**

Two general approaches, batch system and continuous system, have been used for hydride generation. In the most early work, the hydride was most frequently generated in a batch system. In the batch system, an acidified sample and reducing reagent are injected into the hydride generation vessel. The volatile hydrides are generated and collected in reaction vessel before being swept by argon or nitrogen gas into the detection system. Several collection vessels have been used; these include balloon (34, 52), pressure chamber (36, 38, 40, 53, 54) and different designs of glass vessel (55-56). The balloon collection system, which collects the hydride, has never gained widespread acceptance because the acid vapour degrades the balloon surface quickly and results in leakage. The pressurized chamber collection system and different design glass vessels have been used more frequently.

There are three variations of the batch type operation. First, the generated hydride and hydrogen can be swept immediately and directly transported to the detection system. Second, the volatile hydrides are delayed for a few seconds (27), until the generation is completed and then the concentrated hydrides are swept to the detection system. This technique had limited success because of the instability of some hydrides. Third, the hydride is condensed in a 'U'-tube by liquid nitrogen (1, 57) or liquid argon (45). When the tube is warmed, the hydride is vaporized and transferred at once to the detection system (58). The sensitivity from this system is better because the hydride is not diluted with byproduct gases.

With continuous systems, the acidified sample and reducing agent are continuously delivered by a multiple-channel peristaltic pump and are mixed before or upon discharge into the gas-liquid separator. In the gas-liquid separator, hydrides are generated and separated from the liquid waste. Hydride forming elements are subsequently introduced into the detector by a constant flow of purge gas and the waste solution is pumped out. The volatile hydrides can be delivered into the flame, heated quartz cell, or into the plasma and a steady state signal is obtained. Compared with the batch mode, the continuous mode is simpler to

operate, easier to automate and gives better precision over the batch system. Thompson et al. (59) first described a method for the continuous hydride generation system for the determination of arsenic, antimony, bismuth, selenium and tellurium in aqueous solutions. However, the system used a higher forward power (2.7 kW) than commonly used for solution nebulization systems and a higher sample flow rate (9.2 mL/min). In later studies, they (60) improved their system by including a three-channel peristaltic pump connected through a four-way valve to the gas-liquid separator, which enabled the sample to be rapidly switched with a blank and could be operated at 1.25 kW. Ikeda et al. (61) and Nakahara (50) used two sets of gas-liquid separators, consisting of a mixing coil followed by a gas-liquid separator and condensing coil, and second, a gas-liquid separator followed by a condensing coil. Another modification used a four-channel peristaltic pump, the sample and reductant were mixed before discharge in a gas-liquid separator. This design gave smooth and continuous hydride generations and improved signal stability. Hwang et al. (62) found that by continuously pumping waste reagent from the gas-liquid separator the amount of excess hydrogen is reduced and enables the ICP to operate at 1 kW. They (63) also used a mixing 'Y' with cross flow nebulizer and spray chamber as a gas-liquid separator, but the forward power required is higher (1.5 kW). Nowadays the continuous system is the most frequently used method for hydride generation (64).

- **Gas-liquid separator**

The gas-liquid separator is an important component in the continuous hydride generation system. It is employed to separate hydrides from the reaction solution and in order to maintain a stable plasma, different types of gas-liquid separator have been designed to improve the analytical performance. Thompson et al. (60) used 'U'-tube separator in order to delay completion of the reaction between acidified sample and sodium borohydride in a bulb where gas and liquid are separated. Argon gas flows into the bulb and purges hydrides

into the torch. Waste solution flows into a 'U'- tube, then overflows to waste. Pierce et al. (65) and Pyen et al. (8) designed a modified interface vessel, filled with 3 mm o.d. pyrex beads for smooth separation of liquid and gas. Pacey (66) and Barnes (67) used a porous PTFE membrane or microporous PTFE tubing as a gas-liquid separator. Chen et al. (50) used a frit-based gas-liquid separator for stibine generation. The sample and reductant flow into the gas-liquid separator just above the frit, where the waste solution drain from the opposite side. Hydrides are purged by argon stripping gas from below the frit, an additional gas flow from the side arm breaks bubbles and prevents liquid from entering the gas outlet port at the top of the vessel. The development of the gas-liquid separator has been directed towards minimizing the size of the dead volume while maintaining good sensitivity and separation efficiency for reliable results and low relative standard deviation. Brindle and Zheng (68) compared four different designs of gas-liquid separators for the determination of mercury by cold-vapour sequential injection atomic absorption spectrometry. The best results were obtained from an in-house designed frit-based gas-liquid separator and from a Perkin-Elmer FIAS Chemifold system. The same frit-based gas-liquid separator was used for these studies.

- **Detection system**

A hydride generation system is simple and easy to connect with many spectroscopic techniques.

- 1969, Holak (1) used Atomic absorption spectrometry as a detection system with hydride generation.
- 1972, Braman et al. (69) used 1% NaBH₄ solution to generate arsine and stibine and swept the hydrides with helium gas to be determined by d.c. discharge method.

- 1978, Thompson et al. (60) were the first who reported the introduction of hydrides into the ICP-AES for the simultaneous determination of arsenic, bismuth, antimony, selenium and tellurium.
- 1983, Date and Gray (70) first reported the use of hydride generation with inductively coupled plasma mass spectrometry for the detection of arsenic.

A review of hydride generation systems for atomic absorption spectroscopy was presented by Robbin and Caruso (11) in 1979. Nakahara (13) discussed principles and applications for atomic absorption, atomic fluorescence and plasma atomic emission in 1983 and in sample introduction for atomic absorption spectroscopy (25). Campbell (71) in 1992 and recently Yan and Ning Ni (72) in 1994 also reviewed the application for atomic absorption spectroscopy. Recently, Dedina and Tsalev (73) presented a comprehensive review and discussed the fundamental and practical considerations of hydride generation atomic absorption spectrometry. They also include applications and bibliographical references. The application of hydride generation has been extended to plasma emission field, and was comprehensively reviewed by Heitkemper et al. (64) in 1992.

- **Inductively coupled plasma**

The inductively coupled plasma (ICP) is a high performance source for atomic emission spectroscopy for simultaneous multi-element determinations at trace levels. The ICP source as described by Greenfield et al. (74) and by Wendt and Fassel (75), has a range of attractive properties for emission spectrometry. The main advantages are simultaneous multi-element capability, relatively high level of accuracy and precision, low detection limits, wide linear calibration range (typically over five orders of magnitude of concentration), low sample consumption, fast sample throughput and short integration times.

The principle of ICP has been explained in detail in many publications (76-78). An ICP source consists of argon flow gas ionized by an applied radio frequency field typically oscillating at 27.1 MHz or 40 MHz. This field is inductively coupled to the ionized gas by a water-cooled coil surrounding a quartz torch. A sample aerosol is generated by an appropriate nebulizer, then passed through the spray chamber, where big droplets are separated and the remaining aerosol is carried by argon gas into the plasma through an injector tube located within the torch. The high temperature of the plasma (about 8000 K) is available for drying, atomization, ionization and excitation with high efficiency. The emissions from the plasma enters a spectrometer where they are focused on an entrance slit followed by dispersion on a polychromator. The emission spectrum of each element is isolated for intensity measurements. In inductively coupled plasma atomic emission spectrometry (ICP-AES), the variables include forward power, observation height, gas flow rates and torch design.

ICP-AES can operate with a variety of different sample introduction devices. The sample can be a solid, liquid or gas. Flexibility and performance characteristics have made ICP widely acceptable.

- **Hydride generation inductively coupled plasma**

Inductively coupled plasma has been the most widely accepted technique for the simultaneous determination of hydride forming elements. Thompson et al. (59) were the first to report the introduction of hydrides into the inductively coupled plasma for the simultaneous determination of arsenic, bismuth, antimony, selenium and tellurium by sodium borohydride-acid reaction. The hydrides were continuously produced and introduced into the ICP. The sensitivity and detection limits were improved at least an order of magnitude over conventional nebulization. Their system acidified samples with 5 M HCl, which is not suitable for the determination of germanium and tin, so the conditions for these

elements were found and presented in the following paper (79). One problem inherent to hydride generation that has delayed successful application of this method is the gaseous by-products (H_2 , H_2O and CO_2) of the hydride reaction cause instability of signals and extinguish the plasma at low RF power. In order to keep the ICP from extinguishing, Thompson et al. employed high RF power (2.7 kW) for their system.

Fry et al. (45) used liquid argon to condense undesirable by-products from hydride generation for the determination of arsenic with batch system. The RF power is reduced to 1.2 kW. In 1982, Eckhoff et al. (57) was able to reduce the RF power to 1 kW by using liquid nitrogen trap and separated arsine, germane and stibine by Chromosorb 102. Hahn et al. (5) used liquid nitrogen trap with teflon shavings for the separation of hydrogen from arsine, bismuthine, germane, stibine, hydrogen selenide and stannane. Their system used a RF power of only 0.9 kW. In later research, low acid concentration and improved hydride generator design were used. The modified system used a three-channel peristaltic pump connected through a four way valve to the gas-liquid separator (61). This design provided a continuous reaction which improved the stability of the system and enabled the sample solution to be rapidly switched with a blank solution. The system operated at lower power of 1.25 kW and could be automated for simultaneous multi-element determination.

Halicz and Russel (80) simultaneously determined arsenic, antimony, selenium and tellurium in silicate rocks and in sulphide ores by ICP-AES. They minimized the interferences by coprecipitating the sample with iron(III) hydroxide at pH 2.4, so the analytes of interest were separated from matrix.

Walton (81) sequential determination of arsenic, antimony and bismuth in low-alloy steels by hydride generation inductively couple plasma in the presence of KI. The results were significantly different from the certified values, e.g. arsenic in NBS 362 and 364, bismuth in NBS 364. These results were similar to Welz and Melcher (82) who determined the same elements by atomic absorption spectrometry.

Huang et al. (83) developed a nebulizer-hydride generator system for the determination of arsenic, antimony, bismuth, selenium and tellurium at ICP power of 1.4 kW. Large droplets of acidified sample from a pneumatic nebulizer were trapped by the impact wall of a smoking pipe shaped hydride generator, collected in a bowl, and made to react with potassium borohydride. The detection limits (26) for arsenic, antimony, bismuth, selenium and tellurium are 7.5, 8.3, 0.6, 3.3 and 2.0 µg/L, respectively.

Lopez et al. (84) developed the method for the determination of arsenic, antimony, tin, bismuth, selenium and tellurium in lead and refined copper by direct sample solution and hydride generation. They suggested that prior separation of the matrix was necessary to inhibit effect of copper on hydride formation. For lead, it was possible to generate hydrides for arsenic, antimony, bismuth and selenium directly from test solutions.

Schramel and Xu (85) determined arsenic, selenium, antimony, bismuth and tin in biological and environmental samples by HG-ICP-AES without a conventional gas-liquid separator. In addition, they compared two digestion methods, 1) pressurized digestion with nitric acid in a closed vessel and 2) use of a mixture of HNO₃-HClO₄-H₂SO₄ acid digestion in an open system. The results for two certified reference materials, mussel BCR 278 and NIES no.6 showed that the acid mixture digestion method gave better results for the determination of arsenic and selenium, due to complete digestion (Antimony, tin and bismuth were not determined). For soil samples, the results agreed for arsenic and selenium, but antimony, tin and bismuth were out of range. One problem can come from incomplete digestion, so a suitable digestion method is necessary for good accuracy. The pressurized digestion with nitric acid was suitable for the determination of arsenic and antimony in orchard leaves. The reported detection limits (36) were 0.2, 0.9, 0.8, 0.5, 0.2 ng/mL for arsenic, bismuth, antimony, selenium and tin, respectively.

Pretorius et al. (86) reported the simultaneous determination of arsenic, selenium and antimony in water by inductively coupled plasma hydride method. In their system, sample

were acidified with 3 M HCl and reacted with 1 % NaBH₄ and 5% KI. The detection limit (36) were 2 µg/L for arsenic and 3 µg/L for selenium and antimony.

Ozaki and de Oliveira (87) simultaneously determined of arsenic, bismuth and antimony in steels and nickel alloys by coupling a polytetrafluoroethylene phase separator layer to an ICP-AES. A reduction of nickel interference on the hydride was achieved by adding a suitable amount of iron(III) and acid.

- **Prereductants and reagents for reduced interference effects**

Since Smith (88) carried out a general survey of direct interferences by 48 elements on the determination of arsenic, antimony, bismuth, germanium, selenium and tin, a number of papers have been published on interference effects (89-92). Welz and Melcher (93-95) proposed a mechanism of interference which related to precipitation of the interfering elements.

Aggett and Hayashi (96) suggest that the interference occurs in solution via the formation of a soluble species formed. Patrick and Krivan (29) reported the interference of bismuth and tellurium on antimony, arsenic, selenium and tin in the hydride generation stage.

Walcerz et al. (97) studied arsenic, antimony and selenium as analytes in the presence of arsenic, antimony, selenium, tellurium, bismuth, tin and lead as interferences. They used a twin channel continuous flow system that allowed independent generation of hydrides from two solutions, one with and the other without the interfering element. The gaseous hydrides from two channels were then mixed prior to entering the atomization cell. In this way, they were able to differentiate between gas-phase and liquid-phase interferences. Interferences by arsenic, selenium and tin were found to occur in the gas-phase only, but interference by bismuth and tellurium also occurred in the liquid-phase.

In order to reduce the interference effect, various reagents have been used to reduce or eliminate interferences in hydride generation. Most workers separated analyte from sample matrix by coprecipitation techniques with manganese dioxide (98), iron(III) (99) and lanthanum hydroxide (3, 16, 100-103).

Potassium iodide has been used to reduce interference effects and in order to get hydride forming elements into the appropriate oxidation state (3, 8, 16, 81, 104), or to act as a masking agent (6, 8). Schramel and Xu (85) added 2% (w/v) potassium iodide in sodium tetrahydroborate to eliminate interference effect from copper ions. Pretorius et al. (105) found that the antimony signal was more than doubled by adding 5% (m/v) potassium iodide. It also has been used in combination with ascorbic acid for the reduction of pentavalent antimony and arsenic to the trivalent state (106), or in combination with sodium sulfite (107), thiourea (26, 108, 109) and tin (II) chloride (110). However, potassium iodide can only be used in strong acid solution. Most workers used 5 mol L⁻¹ HCl, which can cause corrosion to the metal parts of the instrument. Haring et al. (111) and Stephens (112) reported that, it took 4-5 h to reduce arsenic(V) to arsenic(III) completely at room temperature. Another problem is that potassium iodide solutions are unstable and have to be prepared fresh daily. Moreover, it cannot be used for the determination of selenium because potassium iodide can reduce selenium to the elemental state, which does not react to form a hydride (113).

In the last twelve years, studies have been carried out to reduce interference effects and to enhance signals of interest. Brindle and Ceccarelli (114) used ammonium peroxodisulphate to enhance signal of germanium and reduce interference from transition elements. Ceccarelli (115) also used 3 % cystine to eliminate interference from nickel, cobalt, iron, copper, cadmium and zinc for the determination of arsenic. Reagents such as L-cystine, L-cysteine, penicillamine and thioglycerol have been tried by Boampong, Brindle and Le (116-118). They found that L-cysteine is the best reagent for reduction of interferences and signal enhancement of germanium. Le et al. (9) compared the reducing

efficiency between L-cystine and L-cysteine. They found problems from excessive foaming from L-cystine and from its limited solubility. They reported that L-cysteine is a more convenient reducing agent. Chen et al. (10) used L-cysteine for the prereduction of arsenic(V) to arsenic(III). They found that the rate of reduction by sodium borohydride speeds up in the presence of L-cysteine. The signal was enhanced, sensitivity was improved and interference from transition elements and other hydride forming elements were reduced. Chen et al. (50) also proposed L-cysteine for stibine generation with flow injection atomic emission spectrometry. They indicated that L-cysteine has more advantages in term of using low acid concentrations, low hydrogen production into the plasma and low toxicity. An et al. (119) got similar results and reported that L-cysteine is an effective compound in reducing transition metal interference. Recently, Welz and Sucmanova (51) used L-cysteine as a reducing and releasing agent for the determination of antimony and arsenic by flow injection atomic spectrometry. They found the same advantage of much lower acid and particularly high tolerance limit from interference in the presence of L-cysteine. Their results shows that L-cysteine gave more advantage over the use of potassium iodide- ascorbic acid.

- **Steels**

Fleming and Ide (3) reviewed the effects of trace amount of elements such as arsenic, antimony, bismuth and tin on the metallurgical properties of steel. The presence of arsenic and antimony reduces the ductility of steel and increases brittleness, however, the addition of antimony improves the resistance to corrosion in acidic environments. Bismuth may be added to improve the free machining properties of steel, but if it contains more than 0.0002%, steel may break during cold working (82). Tin can have a deleterious effect on hot workability of steel. The quality of steels depends on trace amounts of these elements which require the appropriate methods for their determination that can give accurate results at high precision. The composition of elements in steel varies from sample to sample and is

caused by different dissolution properties and mutual affects on the determination of hydrides. A suitable method for simultaneous determination of multi-element in steels is necessary which is interference free and can be used at high sample throughput.

Experimental

A. Instrumentation

- **Inductively Coupled Plasma**

A Perkin Elmer model 3300 DV Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) with the Segmented-Array Charge-Coupled Device Detector, controlled by an external computer running ICP WinLabTM software, was used throughout this work. The operating conditions are listed in Table 1.

Table 1. Inductively Coupled Plasma and hydride generation operating conditions

Inductively Coupled Plasma		
Rf power		1300 watts
Plasma argon flow rate		15 L/min
Auxiliary argon flow rate		0.5 L/min
Nebulizer argon flow rate		0.4 L/min
Plasma view type		Axial
View height		15 mm
Purge type		high purge
Hydride generation		
Reducing agent		NaBH ₄ in 0.1M NaOH
Reducing agent flow rate		2 mL/min
Sample flow rate		2 mL/min

The analytical parameters and wavelength selection are shown in Table 2. All of the wavelengths are those recommended by the ICP WinLab™ software. Selection of wavelengths were based upon their sensitivity values and freedom from interference from other hydride forming elements. An alternative wavelength was chosen and analyzed to identify other potential interferences in steel standard reference materials that might affect the preferred wavelength.

Table 2. Analytical parameters and wavelengths selection

Analytical parameters	Wavelength (nm)
Arsenic	As 188.979
	As 193.696
Bismuth	Bi 190.171
	Bi 223.061
Germanium	Ge 209.426
	Ge 265.118
	Ge 303.906
Antimony	Sb 206.836
	Sb 231.146
Tin	Sn 189.927

- Hydride generation

The acidified sample and reductant were continuously pumped into the gas-liquid separator via a 4-channel peristaltic pump (Gilson Minipuls 312) using a 1.14 mm. i.d.(red-red) pumping tube. The drain tube was purple-orange (3.40 cc/min, part 116-0549p17) from Technicon Instrument Corporation, Terrytown, New York.

Three different designs of frit-based gas-liquid separator and a modified Cetac design were used for the continuous hydride generator. All the gas-liquid separators were made in-house by the Brock University glassblower.

Type I frit-based gas-liquid separator, shown in Figure 1, has a volume of approximately 15 cm³. The inlet ports for the sample and reductant are at the same level, just above the frit. The two ports are as close as possible. The sample and reductant mix as soon as they are discharged from the tubes. On the opposite side from the inlet ports is the outlet port for the waste solution, which is 3 mm above the

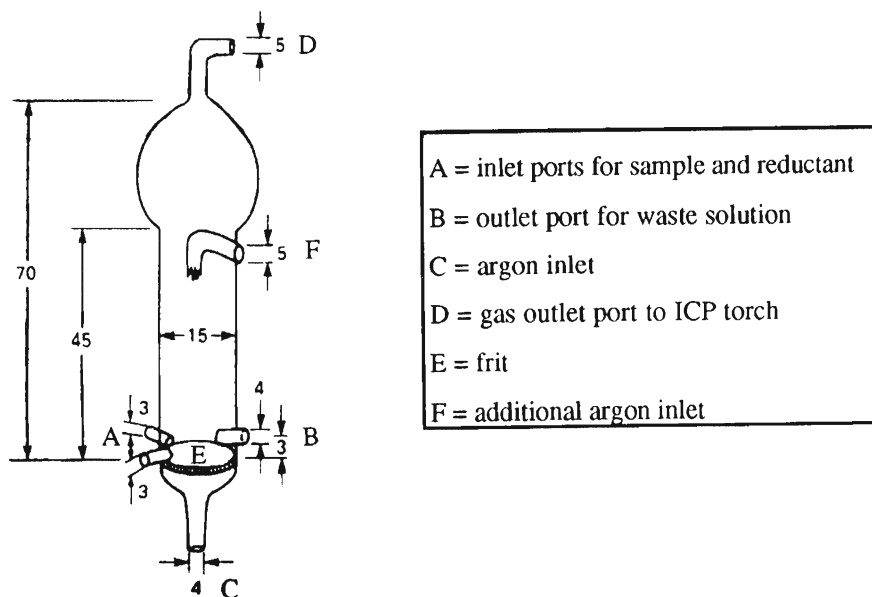


Figure 1. Type I frit-based gas-liquid separator. All dimensions are in millimeters.

frit. Stripping gas (argon) is introduced from below the frit and additional flow is introduced through a side-arm, which is bent down inside the vessel. With this arrangement, the direction of the additional carrier gas flow helps to break any liquid film or bubbles and prevent any liquid from entering the gas outlet port, which is at the top of the vessel.

Type II frit-based gas-liquid separator, shown in Figure 2, has a volume of approximately 63 cm³. The acidified sample and reductant react immediately in the mixing 'Y' before they are discharged from the tube which fits in the inlet port 35 mm above the frit. The mixture flows along the tip and fall on to the frit. The argon flows from the bottom of the gas-liquid separator and passes through the frit. The drain tube above the frit pumps out the waste sample continuously from the gas-liquid

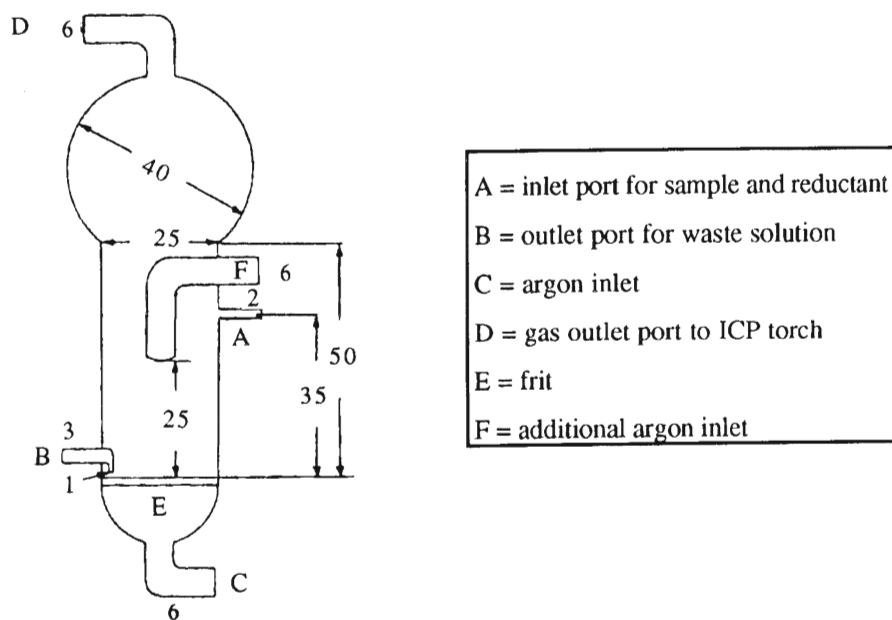


Figure 2. Type II frit-based gas-liquid separator. All dimensions are in millimeters.

separator by the same peristaltic pump. The volatile hydrides are swept out by nebulizer argon gas whose flow is controlled by the software and is directed into the torch for analysis.

Type III frit-based gas-liquid separator, shown in Figure 3, has a similar design as type II, but is smaller. Type III has a volume of approximately 22 cm³. The inlet port is a little bit higher than type II (55 mm above the frit) and the end of the tip is close to the frit (18 mm above the frit). So, the solution mixture can stay longer before it touches the frit and is pumped.

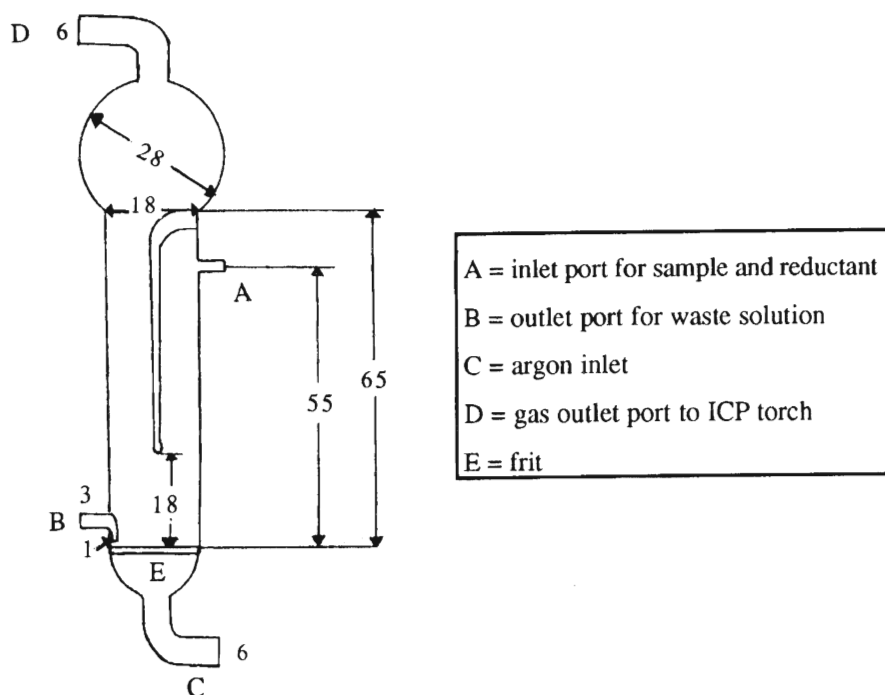


Figure 3. Type III frit-based gas-liquid separator. All dimensions are in millimeters.

Modified Cetac design gas-liquid separator, shown in Figure 4, has a volume of approximately 5.7 cm³. This design has an inlet port at the top of the gas-liquid separator. The acidified sample and reductant are mixed in a mixing 'Y' before being discharged to flow down the glass rod. The argon flows from the bottom and sweeps out the volatile hydrides to the outlet port at the top of the gas-liquid separator where it is transferred directly to the torch of the ICP. The waste is pumped out on the opposite side from the argon inlet.

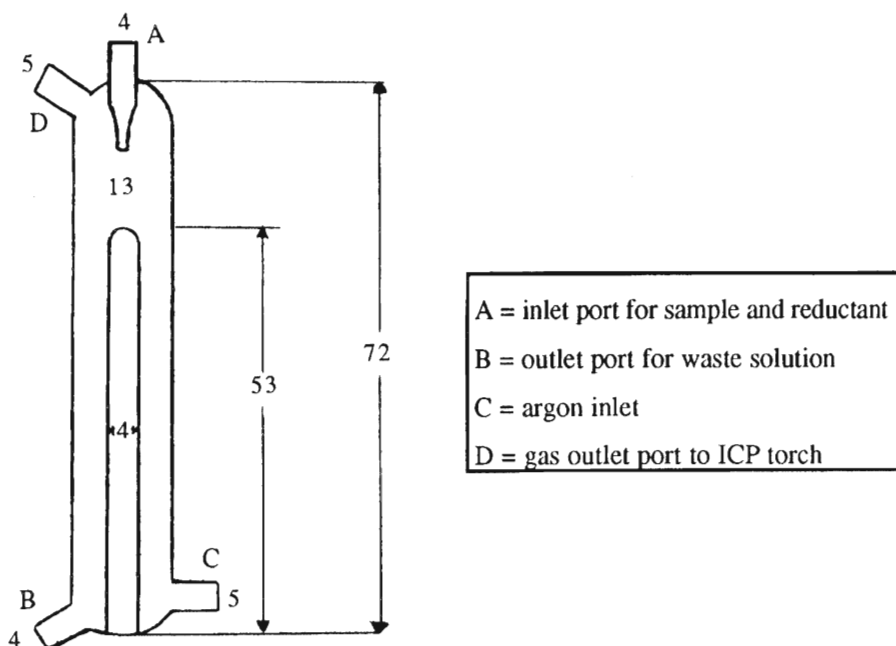


Figure 4. Modified Cetac design gas-liquid separator. All dimensions are in millimeters.

B. Reagents

All reagents used were analytical grade unless otherwise stated, and double de-ionized water (18 M Ω) was used throughout.

- Antimony(V) oxide : Sb₂O₅, lot no. 4144 (J.T.Baker Chemical co., Phillipsburg, N.J., USA)
- Argon, Refrigerated Liquid (PRAXAIR Inc., Mississauga, Ontario, CN)
- Argon, Welding grade (Union Carbide, Mississauga, Ontario, CN)
- Arsenic trioxide : As₂O₃, AR grade (BDH, Poole, England)
- Bismuth shot : Bi, 99.999+% (Johnson Matthey Inc., Seabrook, New Hampshire)
- Germanium Plasma standard : Ge, 1,000 μ g/L, lot no. 701336M (Johnson Matthey Company, Ward Hill, MA, USA)
- Hydrochloric acid : HCl, 32%, GR, lot.no. 216Z288119 (MERCK, Darmstadt, F.R. Germany)
- L-cysteine : C₃H₇NO₂S, lot.no. 128F0378 (Sigma, St.Louis, MO, USA)
- Nitric acid : HNO₃, AR grade 69.0-71%, lot no. B10168-43 (BDH Inc., Toronto, Ontario, CN)
- Nitrogen, Refrigerated Liquid (PRAXAIR Inc., Mississauga, Ontario, CN)
- Sodium borohydride : NaBH₄, approx.98%, lot no.67H3452 (Sigma, St.Louis, MO, USA)
- Sodium hydroxide : NaOH, lot no.24748 (Caledon Laboratories Ltd., Georgetown, Ontario, CN)
- Tin : Sn, lot no.4144 (J.T.Baker Chemical Co., Phillipsburg, N.J., USA)

C. Stock solution and other solutions

1. Antimony stock solution (1,000 mg/L)

1.3285 g of Sb_2O_5 was dissolved in 200 mL of conc. HCl and heated until dissolution was complete and made up to 1 L with deionized water.

2. Arsenic stock solution (1,000 mg/L)

1.3203 g of As_2O_3 was dissolved in 25 mL of deionized water and 50 mL of conc. HNO_3 and heated until dissolution was completed and made up to 1 L with deionized water.

3. Bismuth stock solution (1,000 mg/L)

1.000 g of high purity bismuth metal (99.999 %) was dissolved in 10 mL of conc. HNO_3 until dissolution was complete and made up to 1 L with deionized water.

4. Tin stock solution (1,000 mg/L)

1.000 g of high purity tin metal was dissolved in 200 mL of conc. HCl and left overnight until dissolution was complete and made up to 1 L with deionized water. The solution was stored in a glass bottle that had been presoaked in dil. HCl.

5. Stock solution of standard mixture 100 $\mu\text{g/L}$ of arsenic, 30 $\mu\text{g/L}$ of bismuth, 10 $\mu\text{g/L}$ of germanium, 50 $\mu\text{g/L}$ of antimony and 100 $\mu\text{g/L}$ of tin

1.000 mL of arsenic stock solution, 0.300 mL of bismuth stock solution, 0.100 mL of germanium stock solution, 0.500 mL of antimony stock solution, 0.100 mL of tin stock solution and 0.75 mL of conc. HNO_3 was pipetted into 100 mL volumetric flask and made up with deionized water. This stock solution was used to prepared calibration

curve for steel sample reference material by serial dilution and was made up in 0.12 M HNO_3 and 0.5 % cysteine.

6. Standard mixture 100 $\mu\text{g/L}$ of arsenic, bismuth, germanium, antimony and tin in 0.5% L-cysteine and 0.02 M HNO_3

Pipet 0.2 mL of stock 1,000 mg/L of each elements, added 10.0000 g of L-cystiene and 2.5 mL of conc. HNO_3 (AR grade) make volume to 2 L with deionized water.

7. Sodium borohydride solutions

Sodium borohydride 1-7 % were freshly prepared by dissolving appropriate amount of sodium borohydride in 0.1 M NaOH. This solution is kept in ice bath before use.

8. 1% L-cysteine

10.0000 g of L-cysteine was dissolved in 1,000 mL deionized water. This solution was added in standards and samples to keep 0.5% of L-cysteine in each solution.

D. Determination of arsenic, bismuth, germanium, antimony and tin in steels.

The conditions for the determination of arsenic, bismuth, germanium, antimony and tin in low-alloy steels were investigated with the standard reference materials (SRM) of the National Bureau of Standards (Washington, D.C.). The SRM 362 : AISI 94 B 17 Steel (modified), SRM 363 : Cr-V Steel (modified), SRM 364 : High-Carbon Steel (modified) and 50 c : Chromium-Tungsten-Vanadium Steel.

• Sample dissolution

Approximately 0.1 g of sample was weighted accurately and dissolved in 10 mL of aqua regia (3:1 v/v of HCL: HNO₃) overnight without heat. The solution was diluted and transferred to 1 L volumetric flask. 5.0000 g of L-cysteine were dissolved in deionized water and added to the same flask. The volume was adjusted to approximately 800 mL and the pH was brought to 1.56 with NaOH solution or HNO₃ before being diluted to the mark with deionized water.

• Calibration curve

The calibration curve was prepared by serial dilution of a stock solution of a standard mixture of 100 µg/L of arsenic, 30 µg/L of bismuth, 10 µg/L of germanium, 50 µg/L of antimony and 100 µg/L of tin in a 100 mL volumetric flask. The concentrations of elements for each point are shown in Table 3. All standard solutions were prepared in 0.5 % L-cysteine and at pH 1.56. Each calibration curve was prepared using the same analytical conditions as the sample.

Table 3. Standard solutions mixture preparation for calibration curve for steels

Analytes	Std. 1 ($\mu\text{g/L}$)	Std. 2 ($\mu\text{g/L}$)	Std. 3 ($\mu\text{g/L}$)	Std. 4 ($\mu\text{g/L}$)	Std. 5 ($\mu\text{g/L}$)
Arsenic	5.0	10.0	20.0	50.0	100.0
Bismuth	1.5	3.0	6.0	15.0	30.0
Germanium	0.5	1.0	2.0	5.0	10.0
Antimony	2.5	5.0	10.0	25.0	50.0
Tin	5.0	10.0	20.0	50.0	100.0

Results and Discussion

- **Optimization of the argon flow rate**

The argon flow rate through the gas-liquid separator is an important parameter for the hydride generation system. The argon flow into the gas-liquid separator should be high enough to sweep all hydrides to the ICP torch. But if it is too high it can decrease the signal intensity due to a dilution effect by argon gas. The effects of argon flow rate on signal intensity from four types of gas-liquid separators are shown in Figures 5-8. For multi-element analysis, it can be seen that an argon flow rate of about 400-500 mL/min gave high signal intensity for all elements.

At the same sample flow rate (2 mL/min), the type II frit-based gas-liquid separator gave higher signal intensity than type I, as shown in Figures 5 & 6. Argon flow rate at 400 mL/min gave better relative standard deviation than 500 mL/min for all elements as shown in Figures 9 & 10.

The type III frit-based gas-liquid separator was investigated after the optimization of sample flow rate, so the flow rate of 1 mL/min was used and it gave the same compromise condition for argon flow rate, but the relative standard deviation at 500 mL/min is better than at 400 mL/min.

The modified Cetac design gas-liquid separator was developed at the final part of these studies, so the acid concentration (0.1M HNO₃) used for the optimization of argon flow rate is higher than for the other gas-liquid separators (0.02 M HNO₃), but it gave the same trend for argon flow rate. The relative standard deviation from the modified Cetac design, however, is lower than for all types of frit-based gas-liquid separators examined. This might have some advantage, due to a short residence time of the reactants in the gas-liquid separator.

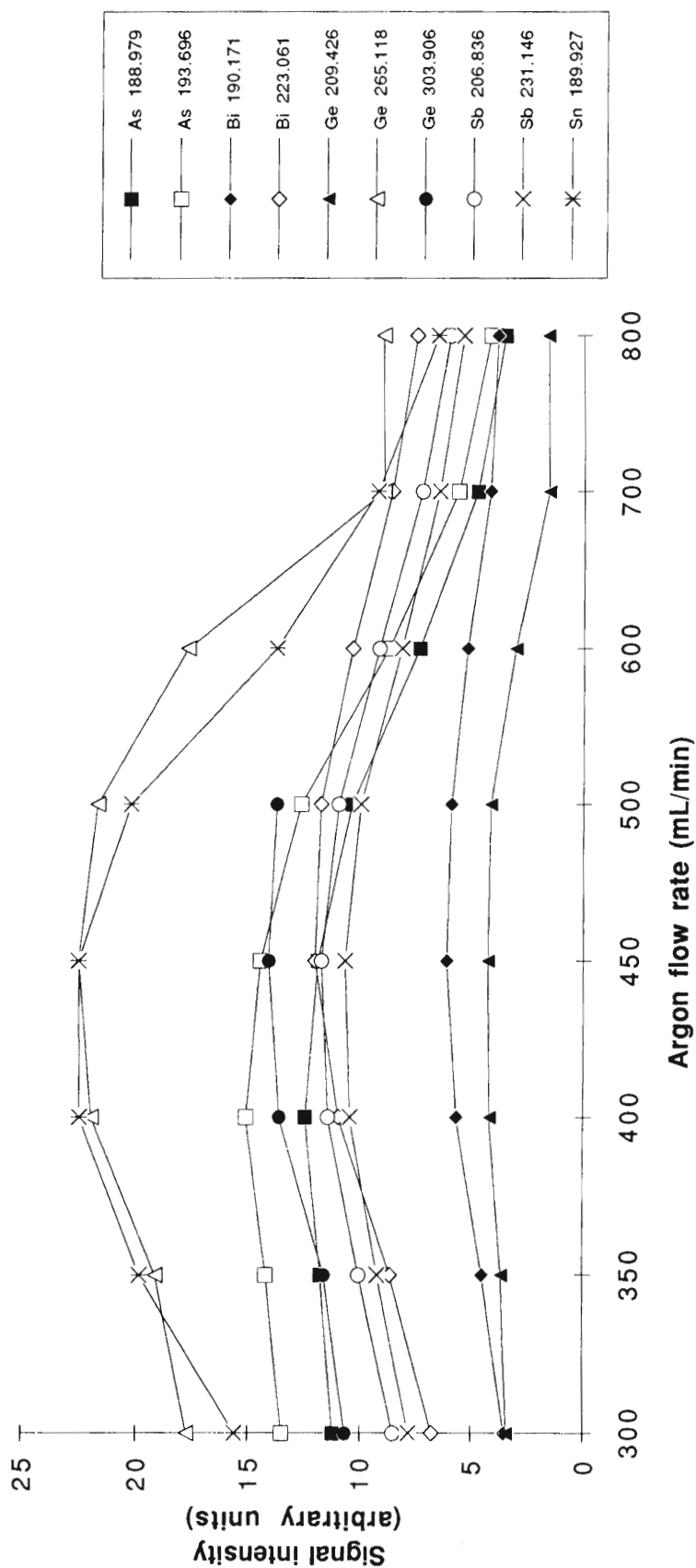


Figure 5. Signal intensity vs. Argon flow rate from type I frit-based gas-liquid separator on standard mixture 100 $\mu\text{g/L}$ in 0.02 M HNO_3 with 0.5% L-cysteine and 1.5 % NaBH_4 in 0.1 M NaOH at sample and reductant flow rate 3 mL/min.

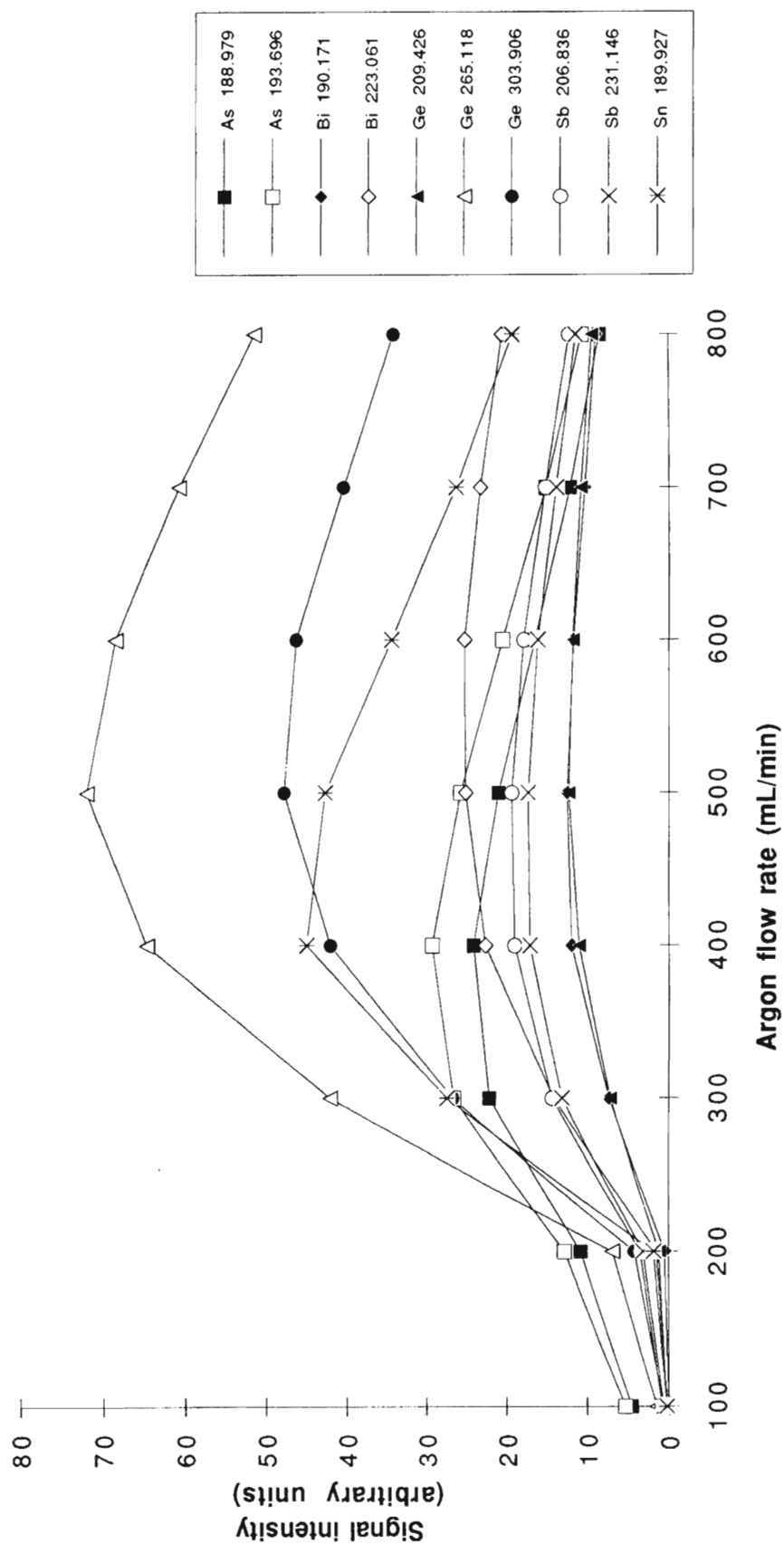


Figure 6. Signal intensity vs. Argon flow rate from type II frit-based gas-liquid separator on standard mixture 100 $\mu\text{g/L}$ in 0.02 M HNO_3 with 0.5% L-cysteine and 1.5 % NaBH_4 in 0.1 M NaOH at sample and reductant flow rate 2 mL/min.

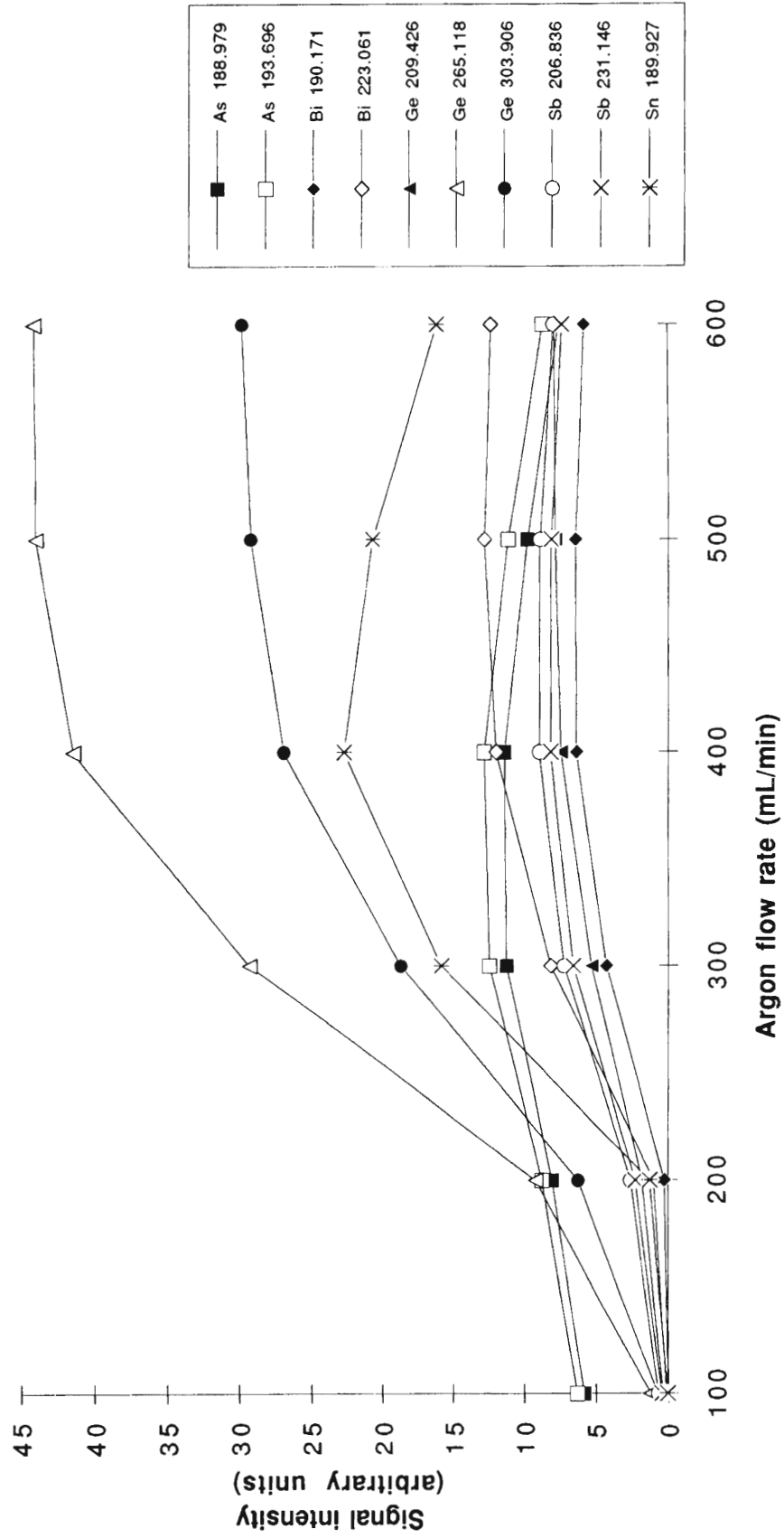


Figure 7. Signal intensity vs. Argon flow rate from type III frit-based gas-liquid separator on standard mixture 100 $\mu\text{g/L}$

in 0.02 M HNO_3 with 0.5% L-cysteine and 1.5 % NaBH_4 in 0.1 M NaOH at sample and reductant flow rate

1 mL/min.

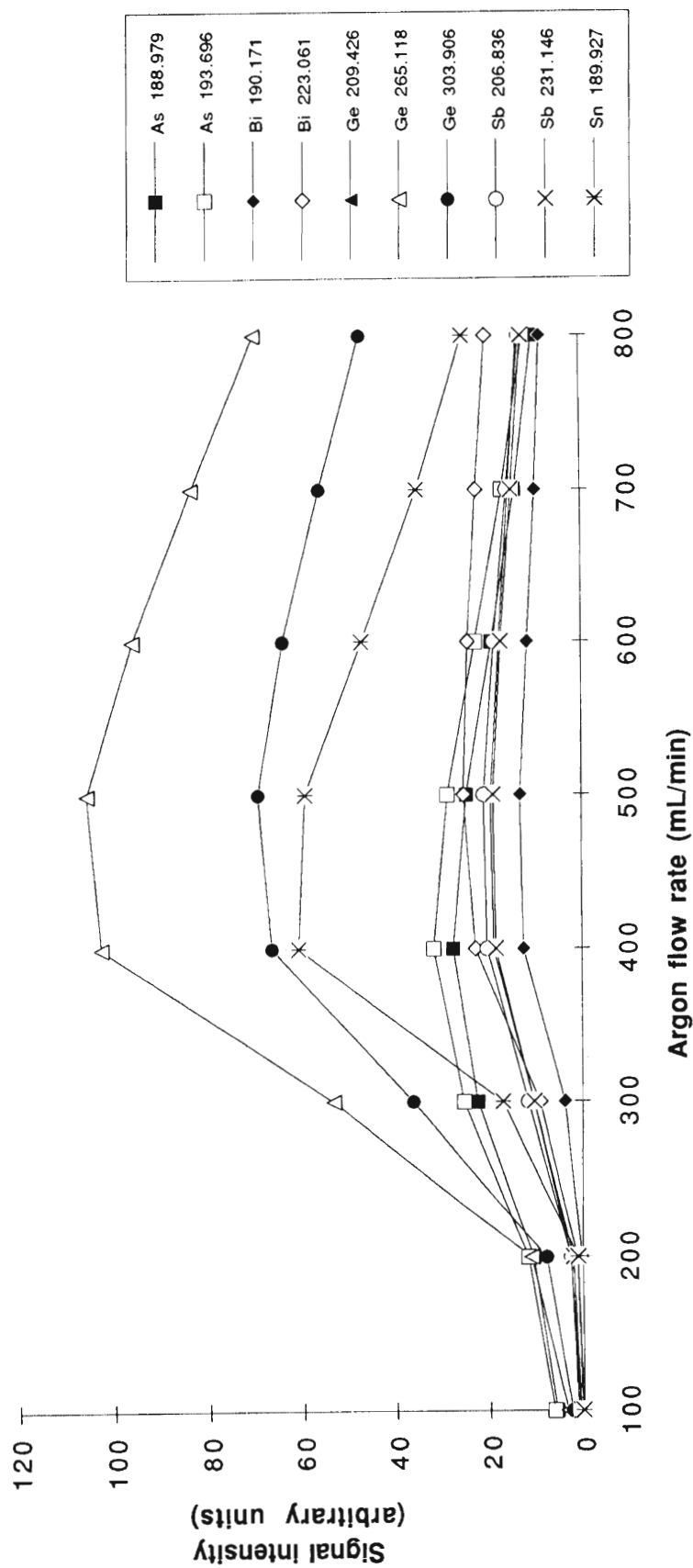


Figure 8. Signal intensity vs. Argon flow rate from modified Cetac design gas-liquid separator on standard mixture 100 $\mu\text{g/L}$ in 0.10 M HNO_3 with 0.5% L-cysteine and 1.5 % NaBH_4 in 0.1 M NaOH at sample and reductant flow rate 3 mL/min.

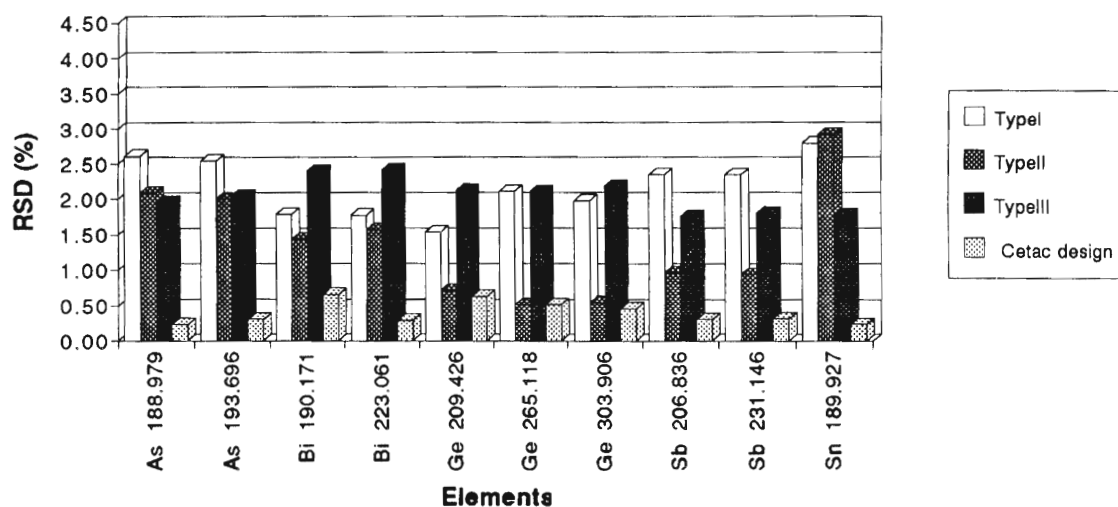


Figure 9. % RSD from different type of gas-liquid separators at argon flow rate 400 mL/min (n=4).

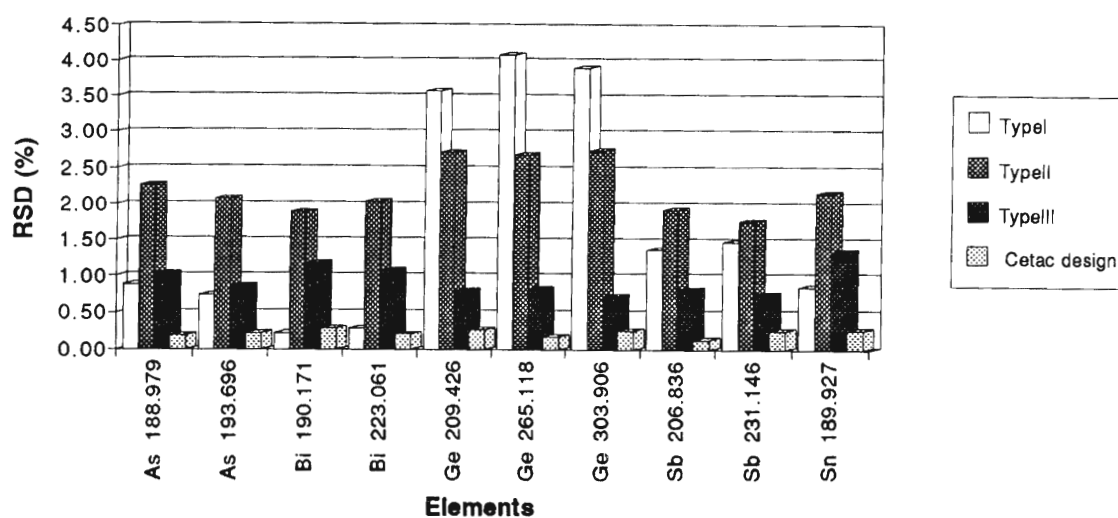


Figure 10. % RSD from different type of gas-liquid separators at argon flow rate 500 mL/min (n=4).

The effect of argon flow rate on signal intensity for arsenic, bismuth, germanium, antimony and tin shows that the signal intensity of tin depends critically on the argon flow rate and that a flow rate at 400 mL/min is best for the determination of tin. Arsenic and germanium are affected by the argon flow rate, but it is not as critical as tin.

• Optimization of sample flow rate

Signal intensity depends on sample flow rate. Increasing sample flow rate will increase signal intensity, but it will consume a large amount of sample solution which is not always available. The sample flow rate was studied to find the minimum sample flow rates needed for each type of gas-liquid separator. Sample flow rates were varied from 0.5 mL/min to 5.0 mL/min by introducing a standard mixture containing 100 µg/L of arsenic, bismuth, germanium, antimony and tin in 0.5 % L-cysteine for type II and type III frit-based and modified Cetac design gas-liquid separators. The results are shown in Figures 11-13 and plots of relative standard deviations are shown in Figures 14-16.

From this experiment we found a problem from the type I frit-based gas-liquid separator. By increasing sample flow rate, bubbles were produced in one side of gas-liquid separator because of a poor glass-to-glass connection so we did not continue our study with type I frit-based gas-liquid separator.

The criterion for choosing sample flow rate is : the lowest sample flow rate that can give low relative standard deviation. Figure 14-16 show that germanium gave high relative standard deviations and fluctuates at all wavelengths of interest. This might occur if the generation of germane has a slow rate at these conditions. The optimum conditions for germanium might be different from other elements of interest, so decisions on sample flow rates were made excluding germanium. For type II frit-based gas-liquid separator, the sample flow rate at 2 mL/min was chosen (%RSD lower than 2%). Sample flow rate for

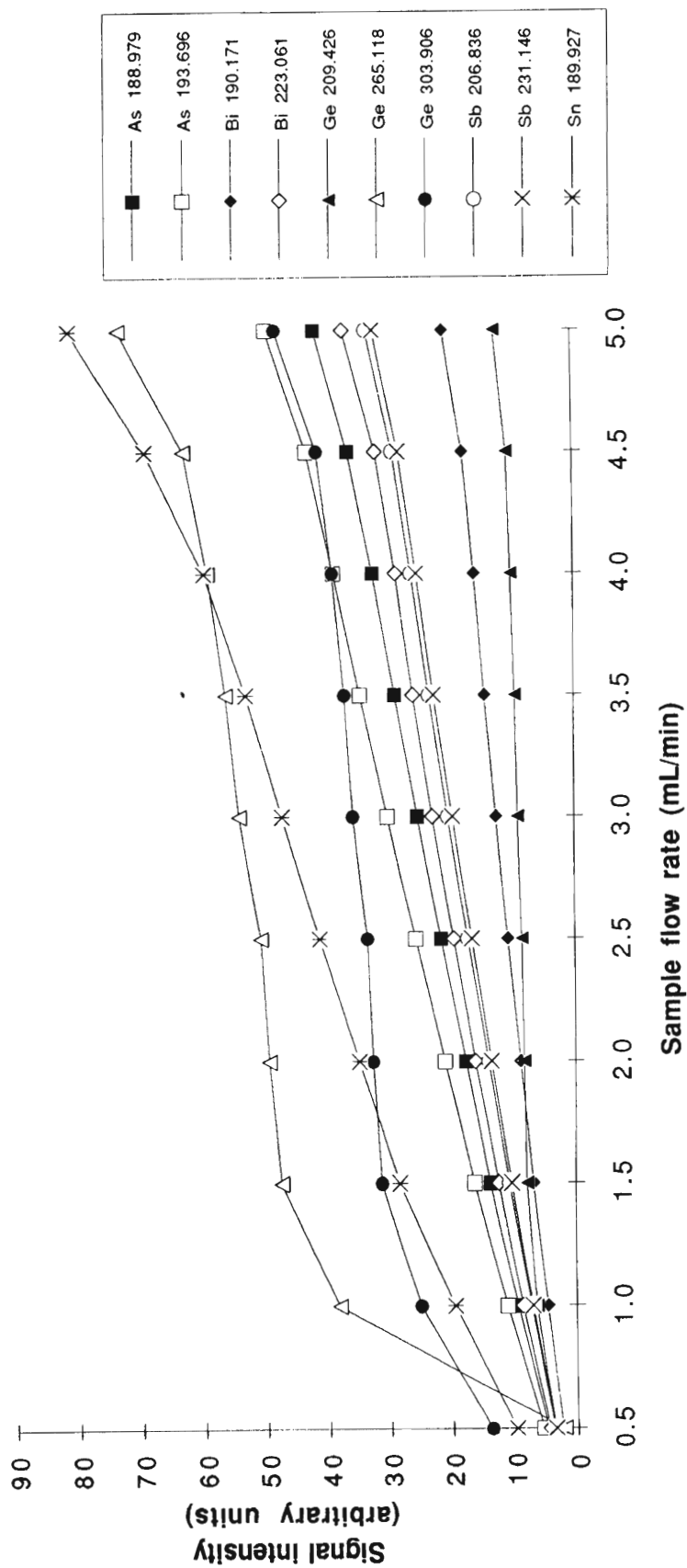


Figure 11. Signal intensity vs. Sample flow rate from type II frit-based gas-liquid separator on standard mixture 100 $\mu\text{g/L}$ in 0.02 M HNO_3 with 0.5% L-cysteine and 1.5 % NaBH_4 in 0.1 M NaOH at argon flow rate 400 mL/min. Reductant flow rates are the same as sample flow rates.

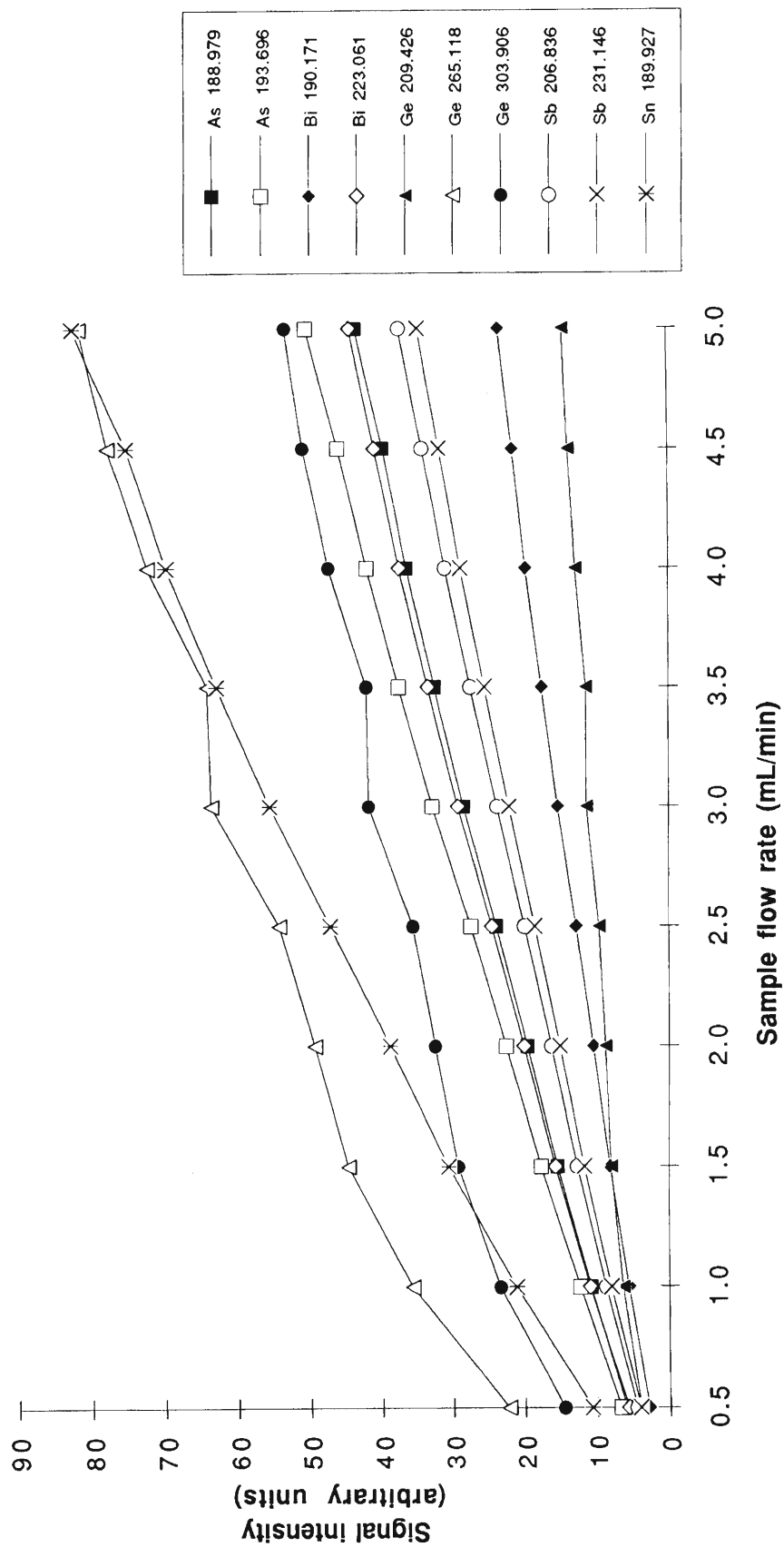


Figure 12. Signal intensity vs. Sample flow rate from type III frit-based gas-liquid separator on standard mixture 100 $\mu\text{g/L}$ in 0.02 M HNO_3 with 0.5% L-cysteine and 1.5 % NaBH_4 in 0.1 M NaOH at argon flow rate 400 mL/min. Reductant flow rates are the same as sample flow rates.

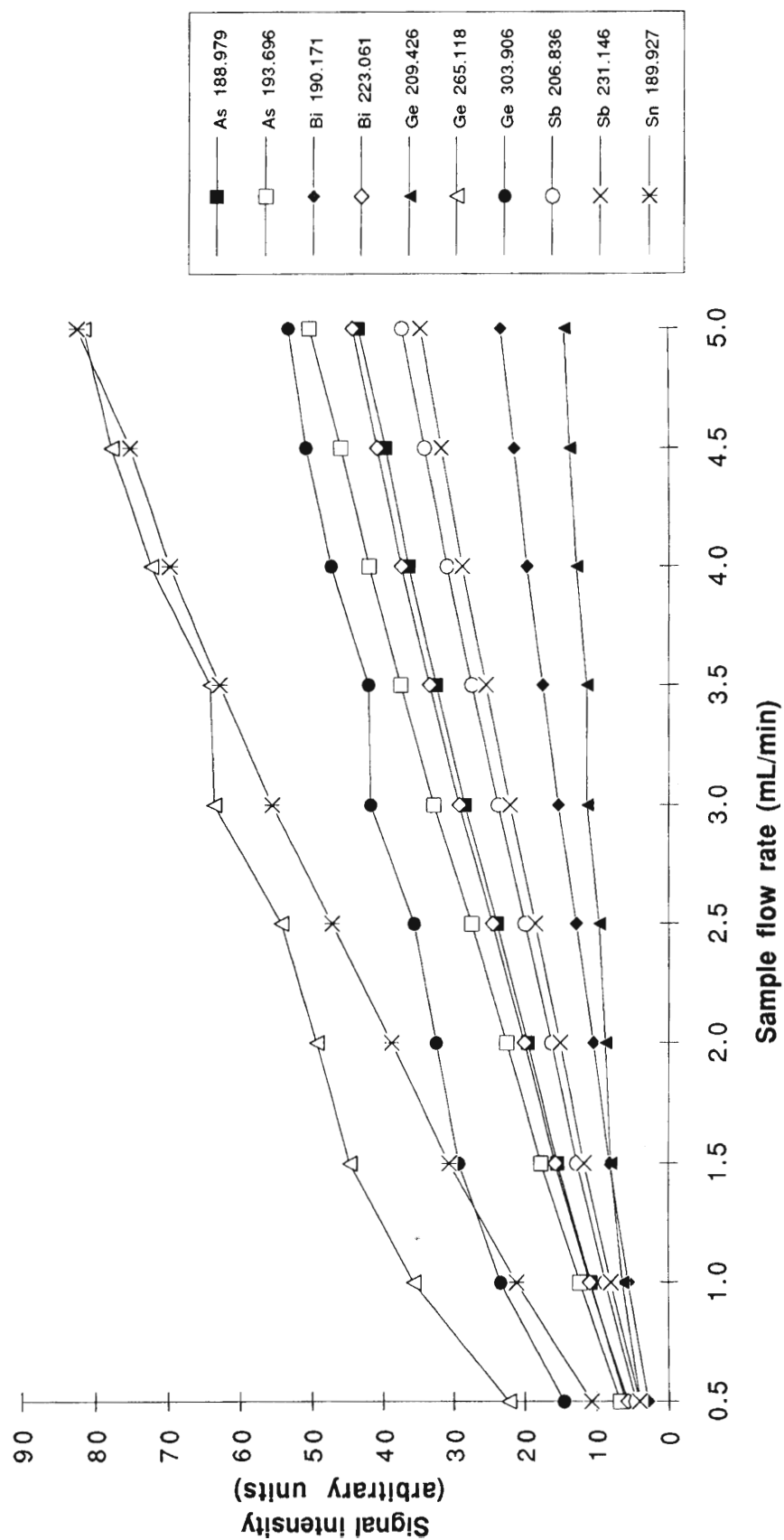


Figure 12. Signal intensity vs. Sample flow rate from type III frit-based gas-liquid separator on standard mixture 100 $\mu\text{g/L}$ in 0.02 M HNO_3 with 0.5% L-cysteine and 1.5 % NaBH_4 in 0.1 M NaOH at argon flow rate 400 mL/min. Reductant flow rates are the same as sample flow rates.

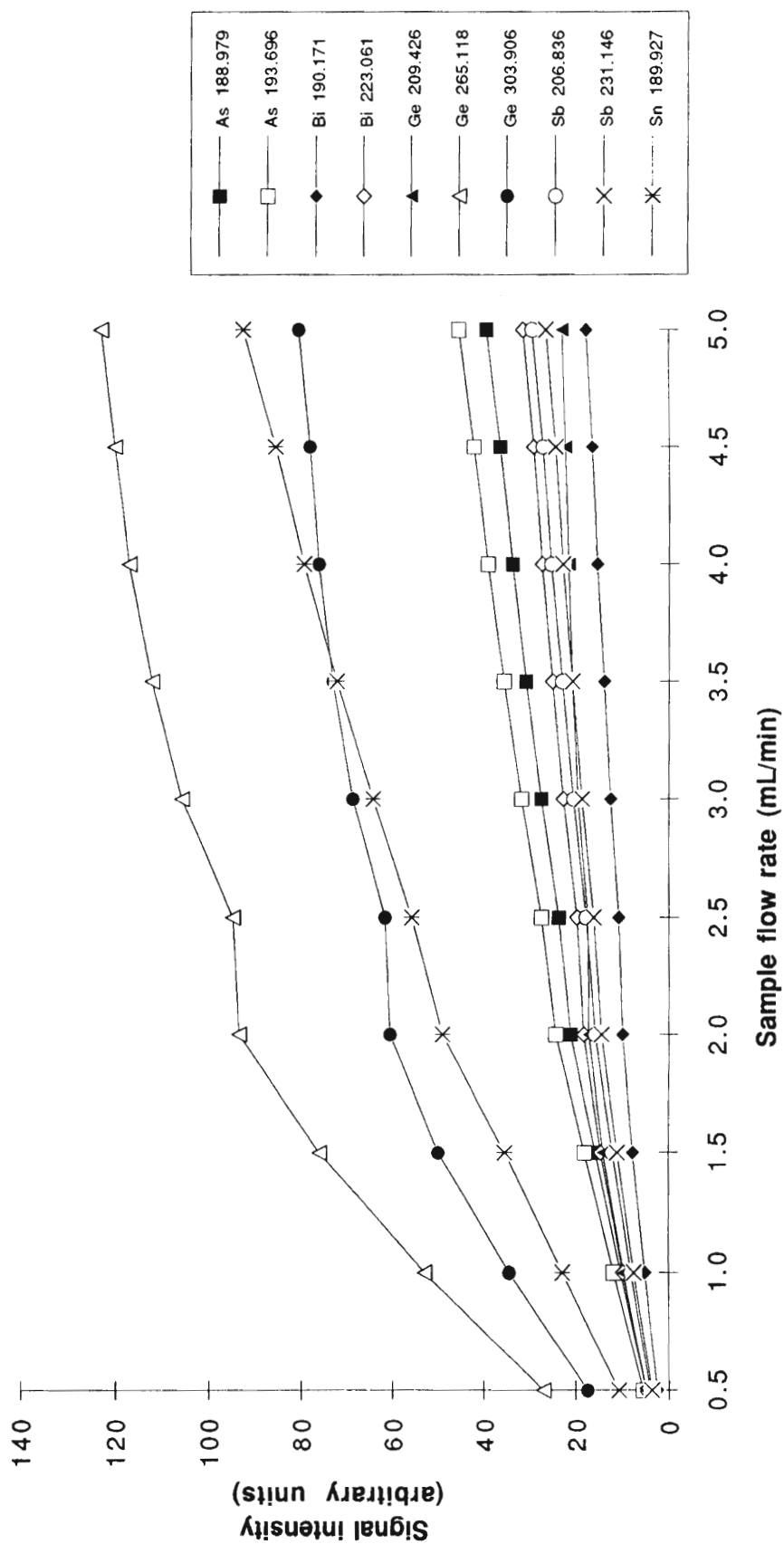


Figure 13. Signal intensity vs. Sample flow rate from modified Cetac design gas-liquid separator on standard mixture

100 $\mu\text{g/L}$ in 0.1 M HNO_3 with 0.5% L-cysteine and 1.5 % NaBH_4 in 0.1 M NaOH at argon flow rate

400 mL/min. Reductant flow rates are the same as sample flow rates.

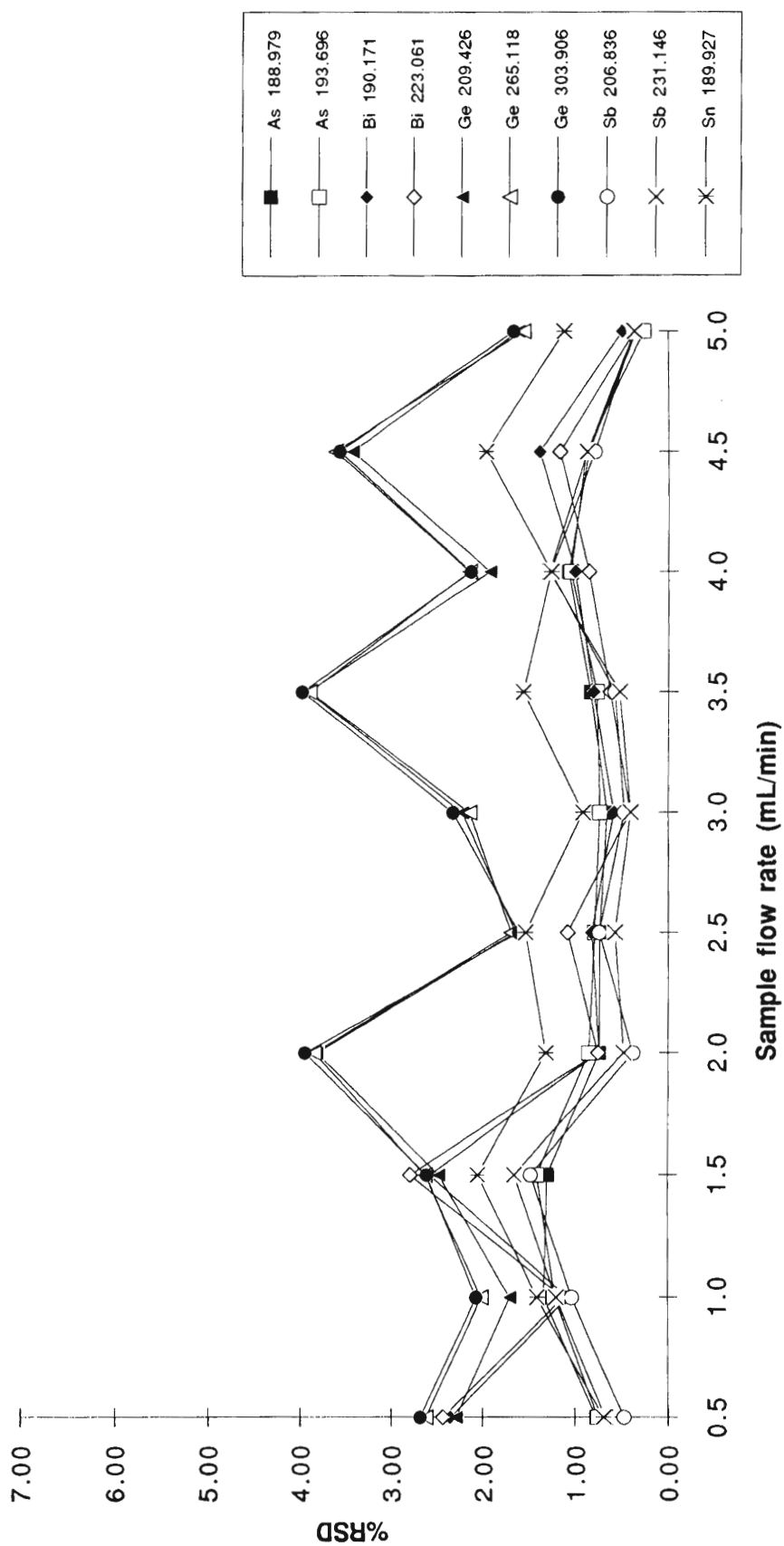


Figure 14. % RSD vs. Sample flow rate from type II frit-based gas-liquid separator (n=4).

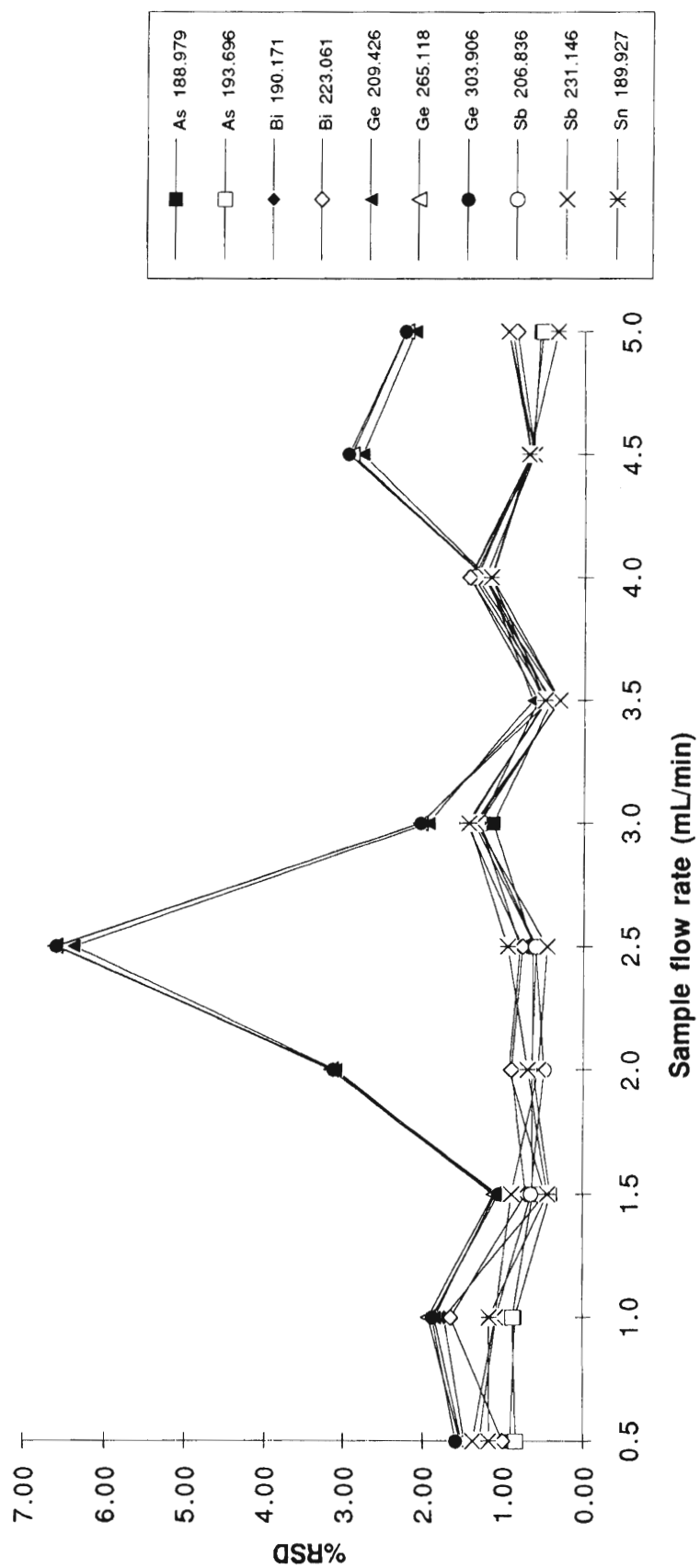


Figure 15. % RSD vs. Sample flow rate from type III frit-based gas-liquid separator (n=4).

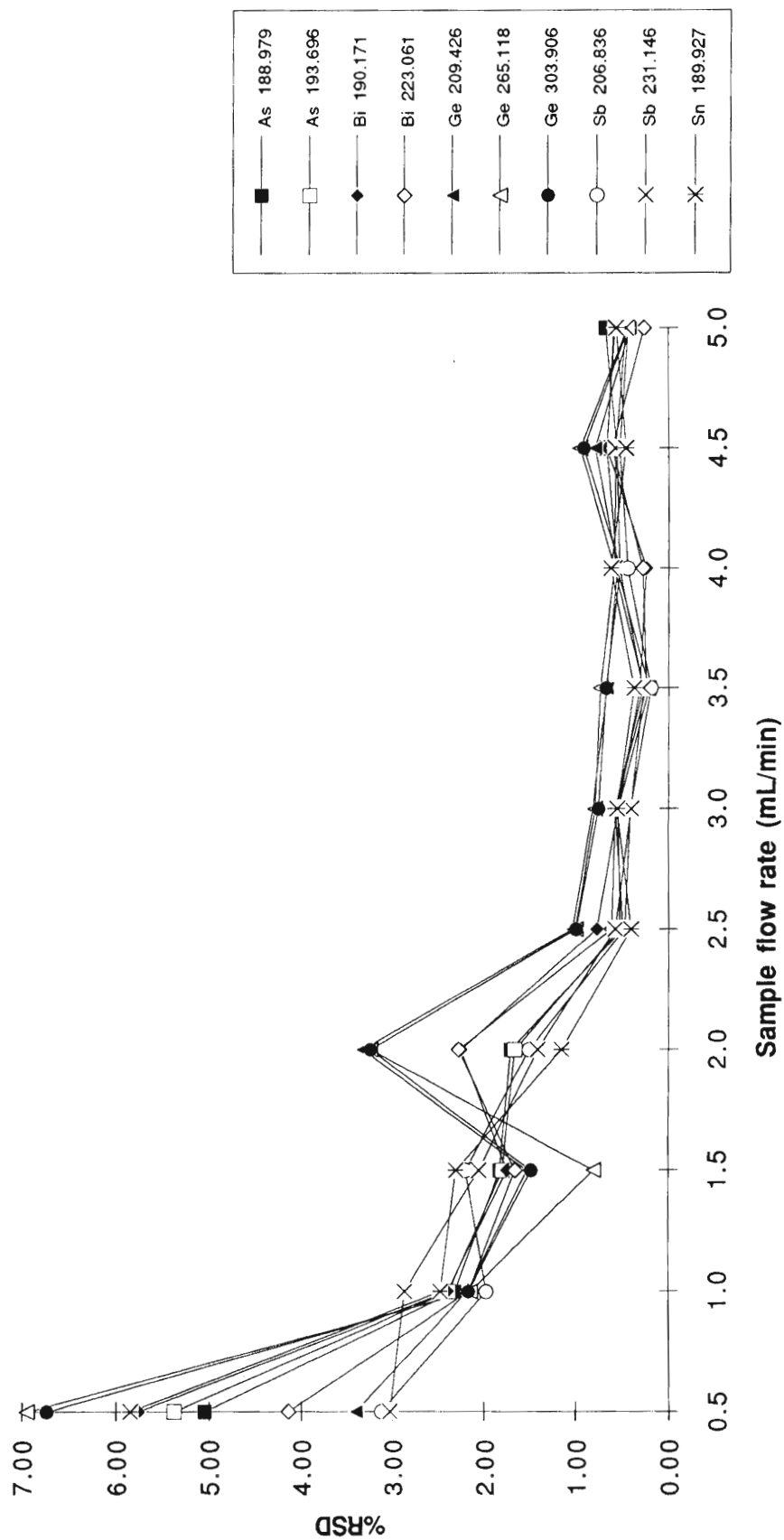


Figure 16. % RSD vs. Sample flow rate from modified Cetac design gas-liquid separator (n=4).

type III frit-based gas-liquid separator and modified Cetac design are 1 mL/min and 3 mL/min, respectively .

Comparing the signal intensity between type II and type III frit-based gas-liquid separator at the same conditions, it can be seen that the type III frit-based gas-liquid separator gave a slightly higher signal intensity than type II at the same sample flow rate, as shown in Table 4. However, the type III frit-based gas-liquid separator was not selected because of a problem from excessive foaming in the small gas liquid separator that tends to overflow into the instrumental line in long term analysis.

The modified Cetac design gas-liquid separator gave lower signal intensity compared with the type II frit- based gas-liquid separator at the same conditions, as shown in Table 5. But, this design gave better relative standard deviation than the frit-based gas-liquid separators, as shown in Figures 9 and 10. Unfortunately, this design was investigated in the final part of this study and modifications to increase delay time for hydride generation, which would improve signal intensity, are necessary. But this design shows promise for the future.

From this point we decided to continue our studies by using the type II frit-based gas-liquid separator at sample flow rate of 2 mL/min and argon flow rate 400 mL/min.

• Optimization of reductant

Sodium borohydride was chosen as the reductant and was prepared fresh daily in 0.1 M sodium hydroxide. To keep stable signal intensity, the solution was kept in an ice bath before and during the analysis to reduce bubbles in the peristaltic pumping tube. The flow rate of reductant was controlled at the same flow rate as sample. Sodium borohydride concentration was varied between 0.5-3.0% m/v to determine the optimum conditions. The results from type II frit-based gas-liquid separator for a standard mixture of 100 µg/L of arsenic, bismuth, germanium, antimony and tin in 0.5 % L-cysteine and 0.02 M nitric acid at

Table 4. Signal intensity from type II and type III frit-based gas-liquid separators at sample flow rate 1 and 2 mL/min in 0.02 M HNO₃ with 0.5% L-cysteine and 1.5 % NaBH₄ in 0.1 M NaOH at the same flow rate as sample.

Analyte and wavelength (nm)	Mean signal intensity (arbitrary units) (n=4)			
	Type II 1 mL/min	Type III 1 mL/min	Type II 2 mL/min	Type III 2 mL/min
As 188.979	9.3	10.8	17.6	19.6
As 193.696	11.1	12.3	21.0	22.6
Bi 190.171	4.6	5.6	8.8	10.4
Bi 223.061	8.6	10.9	16.1	20.1
Ge 209.426	6.4	6.4	8.3	8.7
Ge 265.118	38.2	35.7	49.5	49.4
Ge 303.906	25.0	23.4	32.7	32.5
Sb 206.836	7.2	8.7	13.9	16.3
Sb 231.146	7.0	8.0	13.4	15.1
Sn 189.927	19.5	21.2	35.0	38.8

Table 5. Signal intensity from type II frit-based and modified Cetac design gas-liquid separators at sample flow rate 2 mL/min in 0.1 M HNO₃ with 0.5% L-cysteine and 1.5 % NaBH₄ in 0.1 M NaOH at 2 mL/min.

Analyte and wavelength (nm)	Mean signal intensity (arbitrary units) (n=4)	
	Type II frit-based gas-liquid separator 2 mL/min in 0.1 M HNO ₃	Modified cetac design gas-liquid separator 2 mL/min in 0.1 M HNO ₃
As 188.979	25.8	21.1
As 193.696	30.4	24.3
Bi 190.171	12.2	9.9
Bi 223.061	20.7	18.2
Ge 209.426	19.7	17.1
Ge 265.118	111.1	93.5
Ge 303.906	71.3	60.6
Sb 206.836	17.8	15.7
Sb 231.146	16.6	14.4
Sn 189.927	58.2	49.0

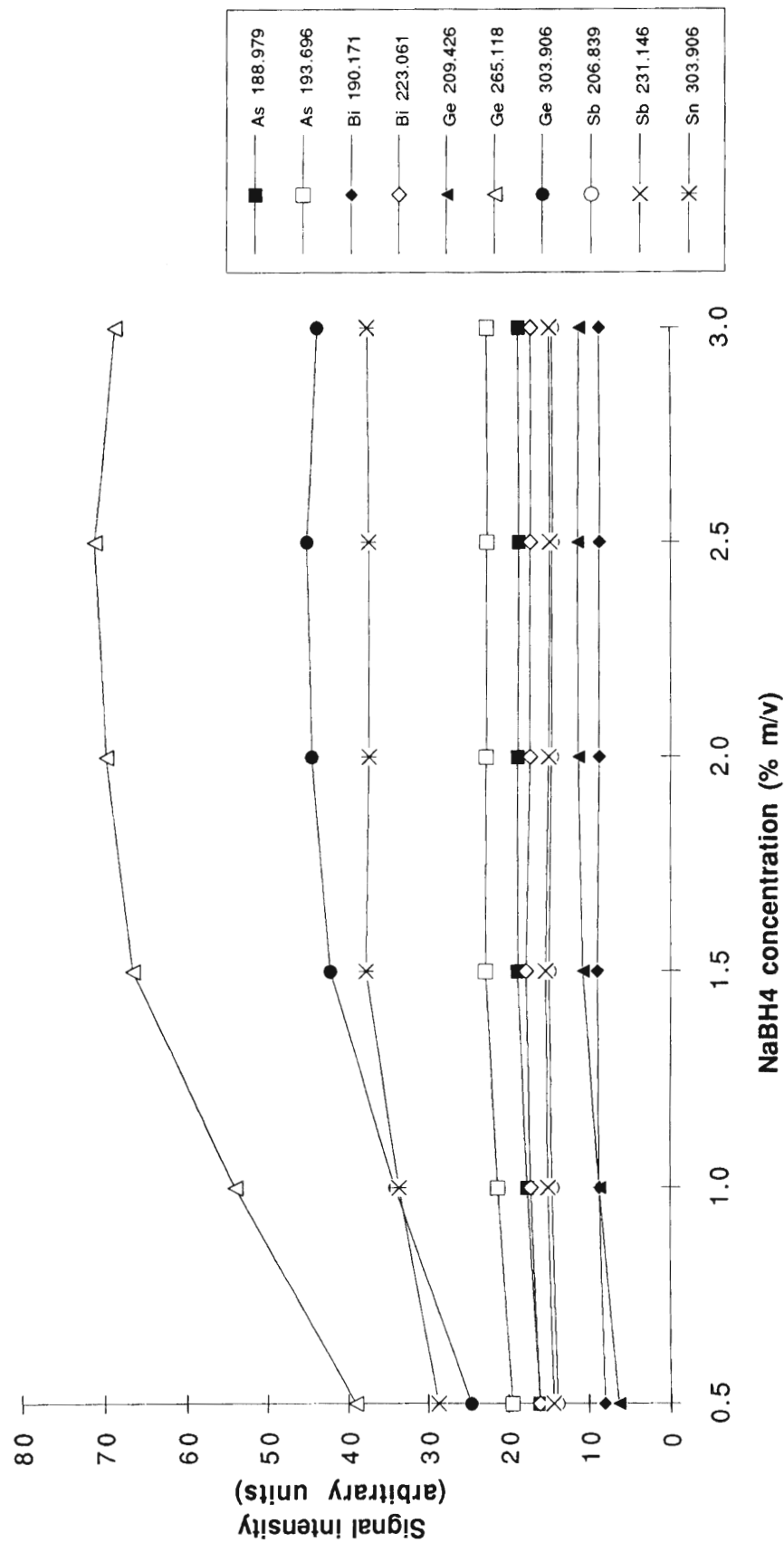


Figure 17. Signal intensity vs. Sodium borohydride concentration from type II frit-based gas-liquid separator on standard mixture 100 $\mu\text{g/L}$ in 0.02 M HNO_3 with 0.5% L-cysteine at sample and reductant flow rate 2 mL/min and argon flow rate 400 mL/min.

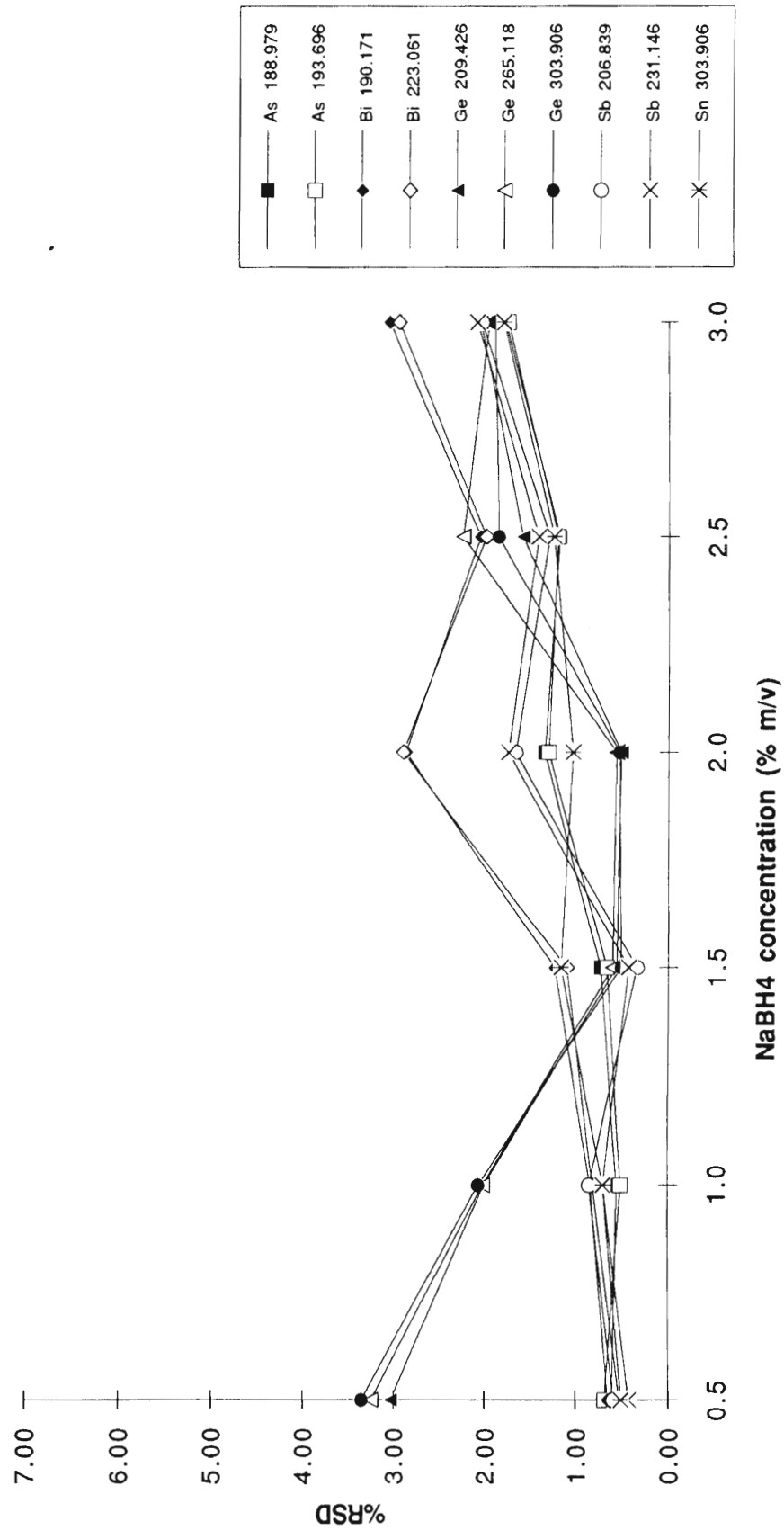


Figure 18. % RSD vs. Sodium borohydride concentration from type II frit-based gas-liquid separator (n=4).

sample flow rate 2 mL/min are shown in Figure 17. The concentration of sodium borohydride in the range of 1.5-3.0% was not critical, but signals tend to be noisier at concentration greater than 1.5%. A plot of the relative standard deviation is presented in Figure 18.

- **Optimization of acid concentration**

All standard solutions and samples in this study were prepared in L-cysteine and acidified with nitric acid. There are several papers which describe successful determinations with low acid concentration in L-cysteine for the determination of arsenic (10, 106, 116), antimony (50, 106), germanium (9, 118) and tin (117). Similar conditions should be appropriate for multi-element determination. In preliminary studies, the same conditions were used (0.02M nitric acid and 0.5% L-cysteine) for comparison of frit-based gas-liquid separators. However, it was recognized that conditions for continuous mode of multi-element analysis by hydride generation inductively coupled plasma with the type II frit-based gas-liquid separator might be different, so the concentration of nitric acid was studied. A standard mixture 100 µg/L of arsenic, bismuth, germanium, antimony and tin in 0.5 % L-cysteine was acidified with nitric acid from 0.01-0.30 M and mixed with 1.5% sodium borohydride in 0.1 M sodium hydroxide in a mixing Y before being introduced into the type II frit-based gas-liquid separator. Results are shown in Figure 19. The signal intensity increased with increasing nitric acid concentration, but drops when the acid concentration is higher than 0.1 M. The relative standard deviations, from Figure 20, show that germanium gave high % RSD at acid concentrations of less than 0.03 M, but the % RSD seems to be better with increased acid concentrations. In contrast, bismuth and tin gave higher % RSD with increased acid concentrations. At acid concentrations higher than 0.1 M, excess hydrogen produced by the decomposition of sodium borohydride caused higher relative standard deviations and extinguished the plasma.

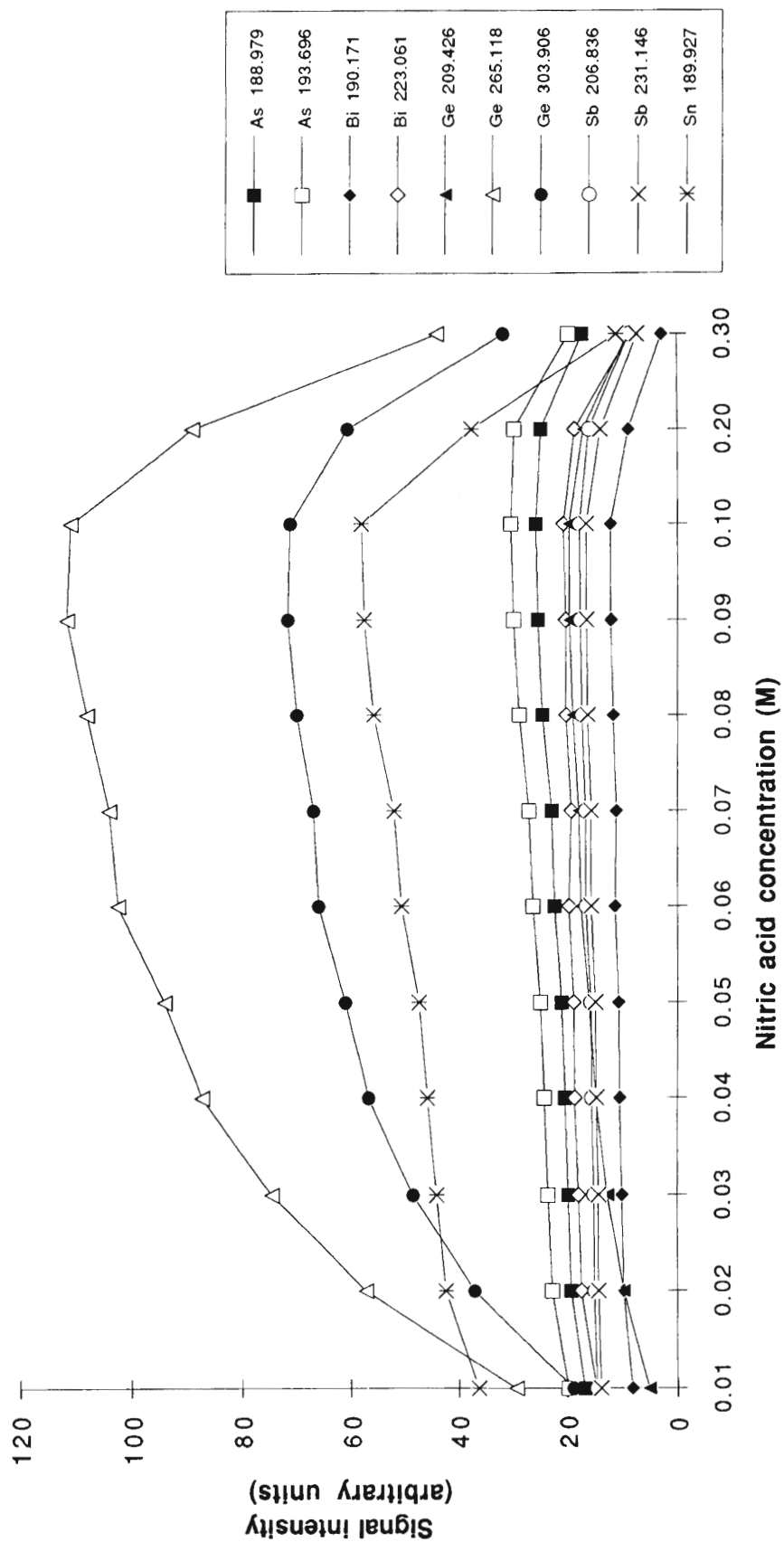


Figure 19. Signal intensity vs. Nitric acid concentration from type II frit-based gas-liquid separator on standard mixture 100 $\mu\text{g/L}$ in 0.5% L-cysteine and 1.5 % NaBH_4 in 0.1 M NaOH at sample and reductant flow rate 2 mL/min, argon flow rate 400 mL/min.

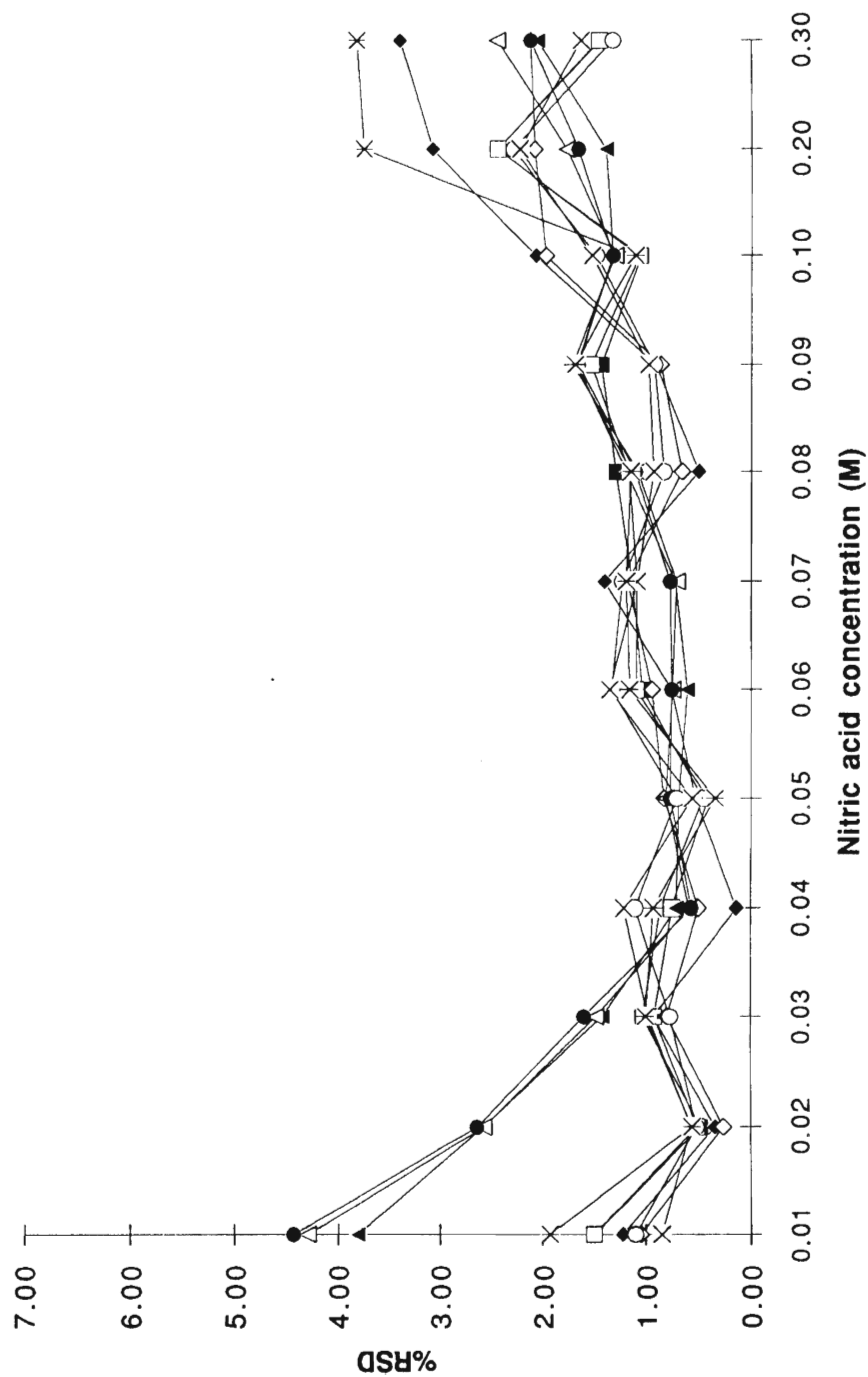


Figure 20. % RSD vs. Nitric acid concentration from type II frit-based gas-liquid separator (n=4).

- **Detection limits**

The detection limits for the determination of arsenic, bismuth, germanium, antimony and tin by hydride generation inductively coupled plasma with type II frit-based gas-liquid separator were determined by linear regression of the results from analysis of 12 replicates of 11 points from a standard mixture of 1-50 $\mu\text{g/L}$ (1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 $\mu\text{g/L}$) at sample flow rate 2 mL/min in 0.10 M nitric acid, 0.5% L-cysteine, 1.5% sodium borohydride in 0.1 M sodium hydroxide and argon flow rate of 400 mL/min. The detection limits, defined as three times of standard deviation of blank, for arsenic, bismuth, germanium, antimony and tin were determined twice, but the second time the detection limits were worse due to the deposition of salt on the ICP window from previous experiments. The detection limits from both experiments are summarized in Table 6. The parameters of the linear regression lines of arsenic, bismuth, germanium, antimony and tin from 12 replicates of each wavelength are shown in Table 7.

Table 6. Detection limits of hydride forming elements by type II
frit-based gas-liquid separator.

Analyte and wavelength (nm)	detection limits ($\mu\text{g/L}$) (April 1998)	detection limits ($\mu\text{g/L}$) (May 1998)
As 188.979	0.2	0.2
As 193.696	0.2	0.2
Bi 190.171	0.2	0.3
Bi 223.061	0.2	0.3
Ge 209.426	0.1	0.3
Ge 265.118	0.1	0.2
Ge 303.906	0.1	0.3
Sb 206.836	0.2	0.3
Sb 231.146	0.2	0.3
Sn 189.927	0.2	0.3

Table 7. Summary of regression data from 12 replicate determinations of each element in standard mixture of 1-50 µg/L of arsenic, bismuth, germanium, antimony and tin (1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 µg/L) at sample flow rate 2 mL/min in 0.10 M HNO₃, 0.5% L-cysteine, 1.5% NaBH₄ in 0.1 M NaOH and argon flow rate 400 mL/min by type II frit-based gas-liquid separator.

Analyte and Wavelength (nm)	April 1998			May 1998		
	Correlation Coefficient	Slope \pm SD (arbitrary units)	Intercept \pm SD (arbitrary units)	Correlation Coefficient	Slope \pm SD (arbitrary units)	Intercept \pm SD (arbitrary units)
As 188.979	0.9993	288.9 \pm 0.6	-199 \pm 19	0.9991	265.5 \pm 0.7	204 \pm 21
As 193.696	0.9995	247.2 \pm 0.5	113 \pm 14	0.9991	314.4 \pm 0.8	-2 \pm 23
Bi 190.171	0.9992	101.1 \pm 0.3	201 \pm 8	0.9986	125.2 \pm 0.4	75 \pm 12
Bi 223.061	0.9993	181.1 \pm 0.4	513 \pm 12	0.9981	216.8 \pm 0.8	403 \pm 24
Ge 209.426	0.9997	192.4 \pm 0.3	312 \pm 9	0.9984	215.7 \pm 0.8	307 \pm 22
Ge 265.118	0.9997	1086 \pm 2	-155 \pm 46	0.9992	1178 \pm 3	-123 \pm 84
Ge 303.906	0.9997	698 \pm 1	-370 \pm 30	0.9989	713 \pm 2	-132 \pm 60
Sb 206.836	0.9995	166.1 \pm 0.3	267 \pm 9	0.9988	245.2 \pm 0.7	252 \pm 22
Sb 231.146	0.9995	156.1 \pm 0.3	144 \pm 9	0.9984	224.7 \pm 0.8	62 \pm 23
Sn 189.927	0.9994	525 \pm 1	950 \pm 32	0.9984	556 \pm 2	650 \pm 57

Determination of arsenic, bismuth, germanium, antimony and tin in standard reference materials (low-alloy steel 362, 363, 364 and tool steel 50 c)

• Dissolution process

In principle, each element has its own best dissolution process, especially with respect to the type and concentration of acid used. It is tedious work to find the optimum dissolution process for each kind of sample which contains different elements at different concentrations. For multi-element analysis in routine laboratory applications, a quick procedure that gives compromise conditions for most elements is necessary. Most published papers in simultaneous multi-element analysis did not include germanium in their determination because germanium is one of the elements which is particularly sensitive to interference effects. In fact, compromise conditions can be used for the determination of arsenic, bismuth, germanium, antimony and tin, as shown in the optimization part. It can be seen that, without matrix effects, germanium gave high sensitivity and low detection limits at 0.1 M nitric acid in the presence of 0.5% L-cysteine when reacted with 1.5 % sodium borohydride in 0.1 M sodium hydroxide. The results from NIST standard reference materials for steels show that germanium might be lost during the dissolution process. Dedina and Tsalev (73) also claim that germanium can be easily lost during sample preparation steps. The values for germanium, however, are only approximate values from heat analysis and are not certified by NIST, but are given as additional information on the composition. So, the dissolution process for the determination of arsenic, bismuth, antimony and tin was carried out with 10 mL aqua regia (3:1 HCl:HNO₃) without heat. Unfortunately, this condition gave low recovery of germanium. The result with the same amount of acid with gentle heat followed by 3 mL of H₂O₂ gave higher recovery (10-30 %)

for germanium, but this condition is not compatible with other hydride forming elements. So, we chose the dissolution process without heat for the determination.

- **Wavelengths selection**

Alternative wavelengths were selected from the wavelengths tables in the ICP WinLab™ software and were analyzed throughout this study. All selected wavelength are shown in Table 2. In principle, an appropriate wavelength is the wavelength which gives high sensitivity and is free from spectral interference, especially from the other hydride forming elements. The most suitable wavelength for each element depends on the type of sample which may contain different levels of matrix elements that cause spectral interference. The results from Table 8 show that arsenic at 193.696 nm line gave better signal intensity and lower % RSD than the 188.979 nm line. Bismuth at 223.061 nm gave higher sensitivity than the line at 190.171 nm, as shown in Table 9. The results from SRM 363 in Table 10, antimony at 206.836 nm gave low results when compared with certified values, so line 231.836 nm was chosen. For tin, only the line at 189.927 nm was selected.

- **Comparison the results with certified values**

The calibration curve is most important for the determination of hydride forming elements in standard reference materials which contain different levels of the analyte and interferences. Successful results can be achieved by comparing the signal intensity of sample with signal intensity of standard mixture at the same concentration range. The calibration curve for low-alloy steels 362, 363, 364 and tool steel 50 c was prepared by varied concentrations of arsenic, bismuth, germanium, antimony and tin, as shown in Table 3. At first, the optimization condition at 0.1 M nitric acid in 0.5 % L-cysteine and 1.5% sodium

Table 8. Comparison of arsenic results at wavelength 188.979 nm and 193.696 nm with NIST certified values.

Sample No. with certified value (% m/m)	NaBH ₄ concentration (% m/v)	Found mean \pm SD (% m/m) (n = 4)	
		As 188.979 (nm)	As 193.696 (nm)
SRM 362 0.092 \pm 0.005	1.5	0.072 \pm 0.001	0.072 \pm 0.001
	5	0.078 \pm 0.001	0.079 \pm 0.001
	6	0.081 \pm 0.001	0.082 \pm 0.001
SRM 363 0.010 \pm 0.005	1.5	0.0078 \pm 0.0002	0.0080 \pm 0.0002
	5	0.0088 \pm 0.0001	0.0089 \pm 0.0001
	6	0.0093 \pm 0.0002	0.0095 \pm 0.0002
SRM 364 0.052 \pm 0.005	1.5	0.0403 \pm 0.0007	0.0404 \pm 0.0007
	5	0.0437 \pm 0.0006	0.0439 \pm 0.0005
	6	0.0449 \pm 0.0005	0.0450 \pm 0.0005
50c 0.022	1.5	0.0207 \pm 0.0002	0.0207 \pm 0.0002
	5	0.0218 \pm 0.0004	0.0219 \pm 0.0003
	6	0.0225 \pm 0.0002	0.0226 \pm 0.0002

Table 9. Comparison of bismuth results at wavelength 190.696 nm and 223.061 nm with NIST certified values.

Sample No. with certified value (% m/m)	NaBH ₄ concentration (% m/v)	Found mean \pm SD (% m/m) (n = 4)	
		Bi 190.696 (nm)	Bi 223.061 (nm)
SRM 362 (0.002) ^a	1.5	0.0021 \pm 0.0001	0.0021 \pm 0.0001
	5	0.0025 \pm 0.0001	0.0023 \pm 0.0001
	6	0.0027 \pm 0.0001	0.0024 \pm 0.0001
SRM 363 (0.0008) ^a	1.5	0.00040 \pm 0.00005	0.00048 \pm 0.00008
	5	0.00041 \pm 0.00005	0.00045 \pm 0.00007
	6	0.00047 \pm 0.00008	0.00054 \pm 0.00006
SRM 364 (0.0009) ^a	1.5	0.00115 \pm 0.00007	0.00118 \pm 0.00007
	5	0.00130 \pm 0.00003	0.00121 \pm 0.00003
	6	0.00143 \pm 0.00008	0.00132 \pm 0.00008
50c NA [†]	1.5	-0.00008 \pm 0.00009	-0.00005 \pm 0.00006
	5	-0.00014 \pm 0.00007	-0.00014 \pm 0.00002
	6	-0.00014 \pm 0.00002	-0.00009 \pm 0.00007

^a Values are not certified.

NA[†] not available.

Table 10. Comparison of antimony results at wavelength 206.836 nm and 231.146 nm with NIST certified values.

Sample No. with certified value (% m/m)	NaBH ₄ concentration (% m/v)	Found mean \pm SD (% m/m) (n = 4)	
		Sb 206.836 (nm)	Sb 231.146 (nm)
SRM 362 0.013 \pm 0.001	1.5	0.0113 \pm 0.0001	0.0113 \pm 0.0001
	5	0.0126 \pm 0.0002	0.0129 \pm 0.0002
	6	0.0127 \pm 0.0002	0.0129 \pm 0.0003
SRM 363 0.002 \pm 0.001	1.5	0.0006 \pm 0.0001	0.0015 \pm 0.0001
	5	0.0007 \pm 0.0001	0.0017 \pm 0.0001
	6	0.0007 \pm 0.0001	0.0017 \pm 0.0001
SRM 364 0.034 \pm 0.001	1.5	0.0341 \pm 0.0005	0.0336 \pm 0.0005
	5	0.0375 \pm 0.0005	0.0376 \pm 0.0004
	6	0.0376 \pm 0.0004	0.0381 \pm 0.0006
50c NA [†]	1.5	0.0018 \pm 0.0001	0.0019 \pm 0.0001
	5	0.0019 \pm 0.0001	0.0020 \pm 0.0001
	6	0.0019 \pm 0.0001	0.0021 \pm 0.0001

NA[†] not available.

borohydride in 0.1 M sodium hydroxide was tried, but the results for arsenic were lower than certified values and also antimony and tin in some cases. The optimization in the presence of matrices might shift the response relative to the standard mixture, so nitric acid and sodium borohydride concentration were varied for steel standard reference material. The results show that at 0.12 M nitric acid in 0.5 % L- cysteine and 5 % sodium borohydride in 0.1 M sodium hydroxide gave better results. The calibration curves are shown in Figure 21 and summary results compared to certified values from NIST standard reference materials are shown in Table 11. It can be seen that, for SRM 363 and 50 c, good agreements with certificate values are achieved for all elements of interest. For SRM 362 and SRM 364, arsenic values were lower than the certified values. These values, however, are in agreement with Walton (81) and also Welz et al.(82), who reported similar results from the same SRMs by hydride generation-atomic absorption spectrometry, as shown in Table 12. Bismuth and antimony show good agreement for SRM 362, but the tin value is a little bit higher. The results from SRM 364 gave similar results to the values from NIST for bismuth and tin, which is a little bit closer than Welz, but antimony gave a little higher value than the others, as shown in Table 12.

Table 11. Summary of results of arsenic, bismuth, germanium, antimony and tin at selected wavelength in steel NIST Standard Reference Materials.

Sample and Analytes	Certified value (% m/m)	Found mean \pm SD(% m/m) (n = 4)		
		1.5% (m/v)	5% (m/v)	6% (m/v)
		NaBH ₄	NaBH ₄	NaBH ₄
SRM 362				
Arsenic	0.092 \pm 0.005	0.072 \pm 0.001	0.079 \pm 0.001	0.081 \pm 0.001
Bismuth	(0.002) ^a	0.0021 \pm 0.0001	0.0025 \pm 0.0001	0.0027 \pm 0.0001
Germanium	[0.002] ^b	0.00007 \pm 0.00003	0.00006 \pm 0.00002	0.00009 \pm 0.00005
Germanium		(0.00060 \pm 0.00008) ^c		
Antimony	0.013 \pm 0.001	0.0113 \pm 0.0001	0.0129 \pm 0.0002	0.0130 \pm 0.0001
Tin	0.016 \pm 0.001	0.0167 \pm 0.0003	0.0205 \pm 0.0003	0.0224 \pm 0.0003
SRM 363				
Arsenic	0.010 \pm 0.005	0.0080 \pm 0.0002	0.0089 \pm 0.0001	0.0095 \pm 0.0002
Bismuth	(0.0008) ^a	0.0005 \pm 0.0001	0.0004 \pm 0.0001	0.0005 \pm 0.0001
Germanium	[0.010] ^b	0.00053 \pm 0.00007	0.00050 \pm 0.00007	0.00058 \pm 0.00006
Germanium		(0.00113 \pm 0.00003) ^c		
Antimony	0.002 \pm 0.001	0.0015 \pm 0.0001	0.0017 \pm 0.0001	0.0017 \pm 0.0001
Tin	0.104 \pm 0.001	0.085 \pm 0.003	0.104 \pm 0.001	0.112 \pm 0.001

^a Values are not certified.

^b Values are the approximate value from heat analysis.

^c Values from dissolution by 10 mL aqua regia with heating and followed by 3 mL 30% H₂O₂

Table 11. Summary of results of arsenic, bismuth, germanium, antimony and tin at selected wavelength in steel NIST Standard Reference Materials (cont.).

Sample	Certified value (% m/m)	Found mean \pm SD(% m/m) (n=4)		
		1.5% (m/v)	5% (m/v)	6% (m/v)
		NaBH ₄	NaBH ₄	NaBH ₄
SRM 364				
Arsenic	0.052 \pm 0.005	0.040 \pm 0.001	0.044 \pm 0.001	0.045 \pm 0.001
Bismuth	(0.0009) ^a	0.0012 \pm 0.0001	0.0012 \pm 0.0001	0.0013 \pm 0.0001
Germanium	[0.003] ^b	0.00013 \pm 0.00003	0.00017 \pm 0.00002	0.00017 \pm 0.00004
Germanium		(0.00058 \pm 0.00003) ^c		
Antimony	0.034 \pm 0.001	0.034 \pm 0.001	0.038 \pm 0.001	0.038 \pm 0.001
Tin	0.008 \pm 0.001	0.0073 \pm 0.0004	0.0088 \pm 0.0002	0.0092 \pm 0.0002
50c				
Arsenic	0.022	0.0207 \pm 0.0002	0.0218 \pm 0.0004	0.0225 \pm 0.0002
Bismuth	NA [†]	-0.0001 \pm 0.0001	-0.0001 \pm 0.0001	-0.0001 \pm 0.0001
Germanium	NA [†]	0.00008 \pm 0.00001	0.00012 \pm 0.00005	0.00011 \pm 0.00009
Germanium		(0.0005 \pm 0.0001) ^c		
Antimony	NA [†]	0.0019 \pm 0.0001	0.0020 \pm 0.0001	0.0021 \pm 0.0001
Tin	0.018	0.0165 \pm 0.0002	0.0191 \pm 0.0005	0.0209 \pm 0.0003

^a Values are not certified.

^b Values are the approximate value from heat analysis.

^c Values from dissolution by 10 mL aqua regia with heating and followed by 3 mL 30% H₂O₂

NA[†] not available.

Table 12. Comparison of the results with NIST certified values and others values.

Results are in % m/m.

Sample and Analytes	Certified value (% m/m)	Found mean \pmSD (% m/m) (n=4)	Walton (81) \pmSD (% m/m) ICP-AES	Welz (82) (% m/m) AAS
SRM 362				
Arsenic	0.090 ± 0.005	0.079 ± 0.001	0.080 ± 0.001	0.08
Bismuth	(0.002) ^a	0.0023 ± 0.0001	0.0024 ± 0.0002	0.003
Antimony	0.013 ± 0.001	0.0129 ± 0.0002	0.012 ± 0.0005	0.013
Tin	0.016 ± 0.001	0.0205 ± 0.0003	-	0.016
SRM 364				
Arsenic	0.052 ± 0.005	0.044 ± 0.001	0.040 ± 0.001	0.042
Bismuth	(0.0009) ^a	0.0012 ± 0.0001	0.0015 ± 0.0002	0.0015
Antimony	0.034 ± 0.001	0.038 ± 0.001	0.033 ± 0.002	0.034
Tin	0.008 ± 0.001	0.0088 ± 0.0002	-	0.006

^a Values are not certified.

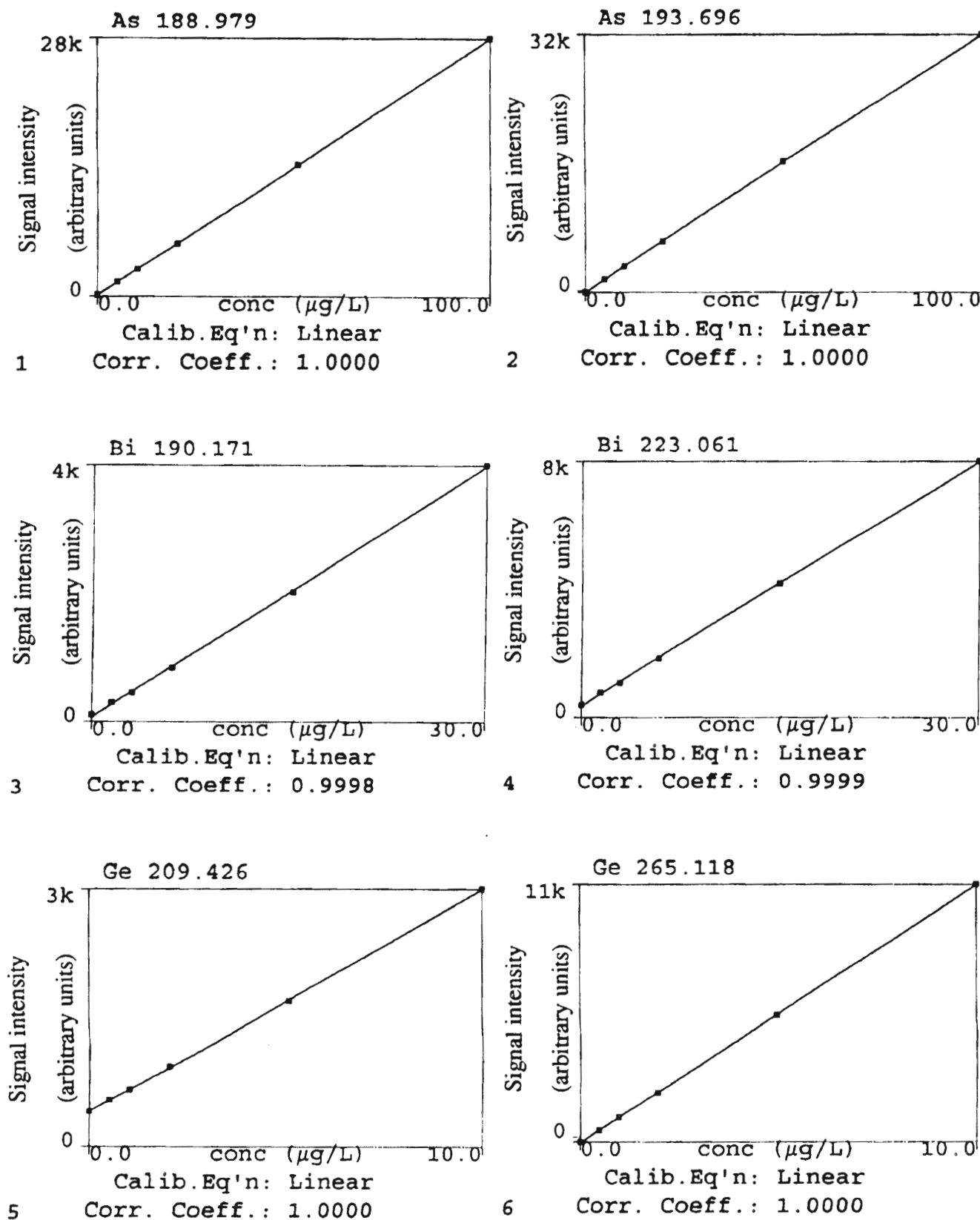


Figure 21. Calibration curve of Standard mixture of arsenic, bismuth, germanium, antimony and tin in 0.12 M HNO₃ with 0.5 % L-cysteine and 5% NaBH₄ in 0.1 M NaOH.

$$K = x 10^3$$

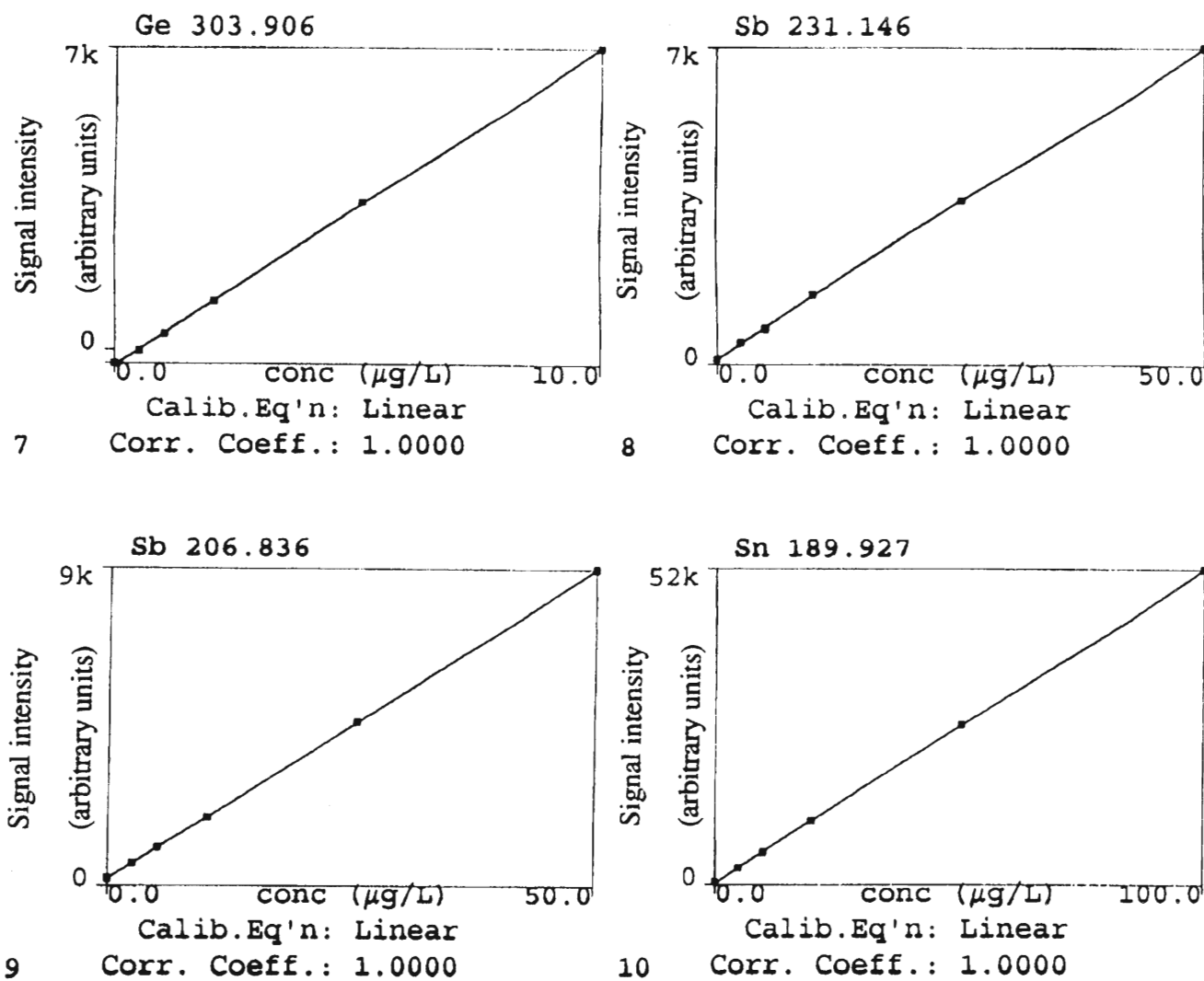


Figure 21. Calibration curve of Standard mixture of arsenic, bismuth, germanium, antimony and tin in 0.12 M HNO_3 with 0.5 % L-cysteine and 5% NaBH_4 in 0.1 M NaOH (Cont.).

$$K = x \cdot 10^3$$

Conclusion

Hydride generation inductively coupled plasma is a good technique for simultaneous determination of hydride forming elements, due to its speed and high sensitivity. The system is simple and it can easily be switched with normal liquid sample introduction. The hydride generator or gas-liquid separator still needs some improvement to minimize the dead volume while providing low relative standard deviation and high sensitivity. From this study, the results indicate that the modified Cetac design gave low relative standard deviations for all elements of interest, but the signal intensity is lower than that of the frit-based design, due perhaps to the short residence time in the gas-liquid separator. Modifying the shape of the glass rod to a coil would permit a longer residence time in the gas-liquid separator and might improve the signal intensity. The design to minimize the volume of gas-liquid separator is required to reduce the sample and reductant consumption. The method developed is useful for the determination of steels at different levels of matrix by calibration with simple aqueous standards.

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