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Determination of Arsenic in a Nickel-based Alloy by Flow Injection Hydride Generation Atomic Absorption Spectrometry Incorporating Continuous-flow Matrix Isolation and Stopped-flow Pre-reduction Procedures*

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A flow system incorporating a microcolumn of strongly acidic cation-exchange resin (Dowex 50W), to achieve continuous-flow matrix isolation, was used to eliminate nickel interference in the determination of arsenic in a nickel-based alloy by flow injection hydride generation atomic absorption spectrometry. A stopped-flow iodide pre-reduction procedure within the matrix isolation unit converted all arsenic present in the sample into As^{III} prior to determination with a tube-in-flame atomizer. The flow injection valve interface between the matrix isolation and hydride generation manifolds allowed separate optimization of each chemistry. After removal of the nickel, the sample stream, flowing at 2.2 ml min⁻¹, was merged first with a stream of 12 mol dm⁻³ hydrochloric acid flowing at 2.2 ml min⁻¹ and then with a stream of potassium iodide solution (30% m/v) flowing at 1.4 ml min⁻¹. For stop times between 5 and 30 s, an average recovery of 97% with respect to As^{III} was obtained. A 400 µl volume of solution was then injected into a water carrier stream (flowing at 11.0 ml min⁻¹), merged with 3.6 mol dm⁻³ hydrochloric acid flowing at 3.2 ml min⁻¹ and a stream of 1.0% m/v sodium tetrahydroborate solution. After passage through a 600 mm open-tubular reactor argon was merged at 400 dm³ min⁻¹ and the arsine separated in a glass U-tube separator. A 0.2 µm polytetrafluoroethylene membrane filter in the gas transfer line removed aerosol droplets with consequent improvement in the performance of the tube atomizer. The procedure was successfully applied to the determination of arsenic in a nickel-based alloy reference material (BCS-346) containing 50 µg g⁻¹ of arsenic for which a sealed-vessel microwave digestion procedure, involving nitric and hydrofluoric acids, was found to produce arsenic in the +5 oxidation state. A characteristic concentration of 2.0 ng ml⁻¹ of arsenic and a limit of detection of 3.9 ng ml⁻¹ of arsenic were obtained with the pre-reduction procedure (which diluted the samples by a factor of 2.7) for a set of operating parameters optimized with respect to interference tolerance and throughput in addition to sensitivity. Under these conditions a sample throughput of 54 h⁻¹ was obtained.

Keywords: Arsenic determination; flow injection hydride generation atomic absorption spectrometry; nickel interference; continuous-flow matrix isolation; stopped-flow potassium iodide pre-reduction

Nickel is known to be a serious interfering element in the determination of arsenic by hydride generation atomic absorption spectrometry (HGAAS).¹⁻⁴ The interference can be reduced by optimization of both acid and sodium tetrahydroborate concentrations^{2,3} and by the use of a variety of complexing and releasing agents.^{2,5,6} A number of ion-exchange resins have been used for matrix isolation, including Chelex 100,^{7,9} Dianion SKIB⁸ and Dowex 50W-X16.⁹

Flow injection (FI) HGAAS, first reported by Åström¹⁰ in 1982, showed improved interference tolerance in comparison with previous batch and continuous-flow methods. Improved interference tolerance in the determination of arsenic by FI-HGAAS has subsequently been reported.¹¹⁻¹³

The use of microcolumn matrix isolation procedures in FI-HGAAS for the removal of interferences has been reported by a number of groups.¹⁴⁻¹⁷ In general, microcolumns have been used in-line within the FI-HGAAS manifold. In a novel matrix isolation system reported previously¹⁷ for the determination of selenium in copper, an independent matrix isolation unit was coupled with the FI-HGAAS manifold through the sample injection valve as interface. The major benefit of the system was shown to be

that the matrix isolation and the FI-HGAAS systems could be optimized independently.

Riby *et al.*¹⁵ described a system for the determination of arsenic in a nickel-based alloy (BCS-346) using continuous-flow HGAAS. Matrix removal was accomplished with an on-line microcolumn of strong cation-exchange material (SCX). A microwave sample digestion procedure was used which was reported to retain arsenic in the analysed sample in the +3 oxidation state.¹⁸

In many instances the sensitivities of arsenic determinations are restricted by the oxidation of arsenic to the +5 oxidation state during sample digestion.¹⁹ The sensitivity of As^V determination in HGAAS has been reported to be inferior to that of As^{III}, particularly in FI-HGAAS,^{20,21} owing to the significantly slower rate of the hydride generation reaction.²² Elimination of the difference in sensitivity between As^{III} and As^V in HGAAS has been obtained by optimization of operating parameters¹¹ and the use of pre-reduction re-agents,^{20,21,23} of which potassium iodide solution has been used most commonly. In most instances the iodide pre-reduction method has been implemented manually prior to analysis, for which reaction times of up to 1 h have been required to achieve quantitative reduction.^{20,21,23} On-line iodide pre-reduction of As^V has been reported in FI-HGAAS.^{12,13} Both of these previously reported methods used a continuously flowing reagent stream of potassium iodide solution (50% m/v). The flow rates were 1.5 and 2.5 ml min⁻¹, respectively which

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represents a consumption of potassium iodide of 60 g h^{-1} on average. Suprapur-grade potassium iodide costs about US\$676.40 per 500 g lot (VWR Scientific, Boston, MA, USA), hence, manifolds which use on-line reduction in a continuous-flow mode are expensive to operate.

In this study an FI method for the determination of arsenic in nickel alloy (BCS-346) by FI-HGAAS was evaluated. The sample is dissolved by a sealed-vessel, microwave-assisted procedure. After passage of the sample solution through the matrix-removal cation-exchange column, a stopped-flow iodide pre-reduction procedure is used to minimize reagent consumption. The arsenic present in the +5 oxidation state after the sample digestion is reduced to As^{III} rapidly on-line prior to introduction into the FI-HGAAS manifold.

Experimental

Apparatus

Unless stated otherwise, the apparatus used was identical with that reported previously.¹⁷ A Philips Scientific SP9 atomic absorption spectrometer equipped with a coded arsenic hollow cathode lamp, operated at 9.0 mA, was used for all determinations. A spectral bandpass of 1.0 nm was used with the 193.7 nm arsenic spectral line and signal damping of 0.5 s. The FI hydride generation manifold reported previously¹⁷ was modified as shown in Fig. 1. A disposable gas line vent filter [VROHO20 hydrophobic $0.2 \mu\text{m}$ polytetrafluoroethylene (PTFE) membrane, PALL] was fitted in-line with the hydride transportation tubing, connecting the gas-liquid separator and the quartz atomization cell. A Seiko digital stopwatch was used to follow the time sequences applied in the analysis procedure. All measurements were made as peak height absorbance. The column was as used previously,¹⁷ namely $50 \times 3.0 \text{ mm}$ i.d. (Anachem), fitted with $0.25 \mu\text{m}$ porous PTFE frits.

All alloy digestions were carried out in a microwave digestion unit (Oxford Laboratories, Model CEM MDS 81D). Poly(propylene) calibrated flasks were used to handle all digested sample solutions.

Reagents

Unless stated otherwise, all reagents were identical with those reported previously.¹⁷ All As^{III} standard solutions were prepared by dilution of a standard solution of arsenic trichloride (Spectrosol, BDH), containing $1000 \mu\text{g ml}^{-1}$ As^{III} . All As^{V} standard solutions were prepared from sodium arsenate (analytical-reagent grade, Fisons). For the investigation of interference and optimization of the matrix isolation procedure, nickel(II) sulphate heptahydrate (AnalaR, BDH) was used to prepare standard solutions. The column packing was the same cation-exchange resin as used previously,¹⁷ namely Dowex 50W-X200, 8% cross-linked (Sigma). For the stopped-flow pre-reduction procedure, potassium iodide (analytical-reagent grade, Fisons) and hydrochloric acid (Spectrosol, BDH) were used. The digestion of the nickel-based reference alloy was carried out using nitric acid (AristaR, BDH) and 40% hydrofluoric acid (AristaR, BDH). The nickel-based certified reference alloy BCS 346 was obtained from the Bureau of Analysed Samples (Middlesbrough, UK).

Digestion Procedure

The method used for the digestion of nickel alloy reference material BCS-346 was as follows.¹⁸ A sample of nickel alloy (1.00 g) was accurately weighed in duplicate into two PTFE microwave digestion vessels. To each vessel were added 20 ml of 4% v/v HNO_3 and 2.5 ml of 40% HF. The same acid

Fig. 1 Schematic diagram of the FI manifold with continuous-flow matrix isolation and stopped-flow KI pre-reduction unit: P1 and P2, peristaltic pumps; S, sample; C, water; A1, A2 and A3, HCl; B, NaBH_4 ; R, KI; W, waste; V_1 , switching valve containing the microcolumn; V_2 , sample injection valve; F, PTFE membrane filter; G, gas-liquid separator; l_R , length of reactor coil; and QTA, quartz tube atomizer

digestion media was added to four other PTFE digestion vessels. The six vessels were capped, equally spaced within the microwave turntable and taken through the 1 h digestion programme (15 min at 30% power, 15 min at 50% power, 30 min at 40% power). Following the digestion programme, the samples were left for 1 h to cool. The vessels were uncapped, their contents transferred into 100 ml poly(propylene) calibrated flasks and diluted to volume with analytical-reagent grade water. Prior to analysis, the digests were further diluted (5+45) to produce working samples containing approximately $1000 \mu\text{g ml}^{-1}$ of nickel. Analysis of the sample solutions was carried out within 24 h of digestion.

Manifold Operation

The hydride generation manifold and matrix-isolation/stopped-flow KI pre-reduction unit were operated according to the optimized variables shown in Table 1. Both As^{III} standard solutions and nickel samples were processed in an identical manner. However, during calibration, column regeneration between standards was not required.

Prior to use, the resin was conditioned by pumping a solution of hydrochloric acid (1.2 mol dm^{-3}) through the column for approximately 5 min at a flow rate of 2.2 ml min^{-1} . After column conditioning and washing, a sample or standard solution was introduced by continuous pumping. In order to fill the void volume of the column, pump tubing and sample injection loop, the column eluent was pumped continuously for a period of 60 s, along with the other reagent streams applied in the matrix isolation/stopped-flow pre-reduction unit. The pump controlling the matrix isolation/stopped-flow pre-reduction unit was stopped for a period of 15 s, thus trapping sample and pre-reduction reagents within the sample loop of the injection valve. The injection valve was activated to introduce its contents into the hydride generation manifold. The injection valve was returned to the load position, the pump restarted and the sampling process repeated to give triplicate determinations of either standard or sample. After triplicate injections of a sample solution, the microcolumn was regenerated (using HCl) and the sample line washed

Table 1 Optimized variables for FI-HGAAS manifold with continuous-flow matrix isolation and stopped-flow KI pre-reduction. Injection volume, 409 μl ; reactor coil length, l_R , 600 mm (0.8 mm i.d.)

Reagent	Concentration	Flow rate/ml min ⁻¹
<i>Hydride generation AAS—</i>		
Water carrier	—	11.0
HCl (A3)	3.6 mol dm ⁻³	3.2
NaBH ₄	1.0% m/v	3.2
Ar	—	400
<i>Continuous-flow matrix isolation—</i>		
Sample	<1000 $\mu\text{g ml}^{-1}$ Ni	2.2
HCl (column regenerant, A1)	1.2 mol dm ⁻³	2.2
<i>Stopped-flow KI pre-reduction—</i>		
KI	30% m/v	1.4
HCl (A2)	12 mol dm ⁻³	2.2

Table 2 Summary of the sampling procedure for matrix isolation and stopped-flow KI pre-reduction including timing sequences

Timing sequence (t)/s	Operation
0	V _S * water pumped <i>via</i> column
10	V _S , sample pumped <i>via</i> column
70	V _I † activation (load position)
80	Pump stopped
95	V _I , activation (inject position)
105	Pump started
	V _I , activation (load position)
	Procedure repeated to give triplicate injections
165	V _B ‡ HCl regenerant pumped <i>via</i> column
	Water pumped <i>via</i> sample line
200	V _S * water pumped <i>via</i> column
	Procedure repeated $t=0$

*V_S, Valve containing column in sampling configuration.

†V_I, Sample injection valve.

‡V_B, Valve containing column in bypass configuration.

with de-ionized water. For column regeneration, hydrochloric acid (1.2 mol dm⁻³) was pumped continuously through the microcolumn, in the direction opposite to that of the sample flow, at a flow rate of 2.2 ml min⁻¹ for 30 s. Following the short period of regeneration, the column was switched back in-line and the sampling procedure repeated. During the transfer of the sample uptake tube from sample to de-ionized water and back, the pump was stopped in order to prevent the introduction of air into the microcolumn. The hydride generation manifold was operated continuously throughout the whole procedure, independently of the matrix isolation/stopped-flow pre-reduction unit. A summary of the sample procedure including timing sequences is given in Table 2.

Method Development

The FI-HGAAS manifold and matrix-isolation/stopped-flow KI pre-reduction unit were optimized independently using a univariate approach.¹⁷ Use of a simplex optimization method was considered inappropriate owing to day-to-day variations in sensitivity, caused mainly by variations in the condition of the atomization cell, which would make this method impractical, as discussed by Bax *et al.*²⁴ The FI-HGAAS manifold was optimized, with the PTFE membrane filter disconnected, unless stated otherwise using a 20 ng ml⁻¹ As^{III} standard solution. In obtaining the optimum variables, although sensitivity was of prime concern, consideration was also given to precision, interference tolerance, system reliability and throughput capability. For the matrix isolation manifold, the retention of nickel on the

column as a function of pH was studied. The capacity of the column was assessed by pumping a 1000 $\mu\text{g ml}^{-1}$ nickel standard solution through the column and continuously monitoring the column eluent by flame AAS.¹⁷ For the pre-reduction process, the effects of stop time, potassium iodide concentration and hydrochloric acid concentration were evaluated. For the hydride generation manifold, the effect of cell pre-treatment, argon flow rate, reactor coil length (l_R , see Fig. 1), the water carrier flow rate, hydrochloric acid flow rate and concentration, the sodium tetrahydroborate concentration and flow rate and the sample volume were all studied. In addition, the interference tolerance of the hydride generation manifold to nickel was evaluated and the possible benefits of the insertion of an aerosol filter into the gas transfer line was investigated.

Results and Discussion

Optimization of FI Hydride Generation Manifold

The performance of the system was significantly affected by the condition of the silica atomization T-cell. The performance characteristics varied from one cell to another, depending on the age and analytical history. Conditioning of the T-cell silica surface by HF etching^{17,25} was found to be beneficial, particularly for unused and contaminated T-cells. Processing high concentrations of As^{III} did not produce any significant increase in performance, in contrast to results obtained previously for the determination of selenium.¹⁷ An efficient method for conditioning of the atomization T-cell was found to be heating in a fuel-rich air-acetylene flame. In particular, after HF etching, the sensitivity was observed to be improved significantly by heating the T-cell within a fuel-rich air-acetylene flame (air flow setting 28; acetylene flow setting 22) for a period of up to 5 min, with the HGAAS manifold connected and running. At the start of each analysis, this conditioning procedure was implemented to optimize the sensitivity and precision. Following conditioning, all determinations were made with a fuel-lean air-acetylene flame (air flow setting 28, acetylene flow setting 15), which was found to be the optimum with respect to both sensitivity and precision. Possibly the conditioning procedure removes active sites on the silica surface and so prevents recombination of radical species and analyte dimerization.^{25,26}

The effect of argon carrier gas flow rate over the range 150–600 ml min⁻¹ was studied. Increasing the argon flow rate caused a decrease in peak height absorbance but an improved rate of hydride transport and reduced peak broadening, culminating in an improved throughput capability. Below 400 ml min⁻¹, the precision was observed to deteriorate (RSD 2.0–4.4% for 20 ng ml⁻¹ As^{III}, based on six replicate determinations). An optimum argon flow rate of

400 ml min⁻¹ was chosen on the grounds of precision and throughput whilst retaining adequate sensitivity (85% of the optimum value which was obtained at 150 ml min⁻¹).

The effect of reactor coil length (l_R , Fig. 1) on As^{III} sensitivity over the range 100–1000 mm (0.8 mm i.d.) is shown in Fig. 2. An increase in peak height absorbance was observed with increasing reactor coil length. An optimum length of 600 mm was chosen after consideration of throughput capability and interference tolerance.¹⁰

The relationship between the flow rate of aqueous carrier solution and the resulting peak height absorbance is shown in Fig. 3. To achieve maximum sensitivity it was evident that the flow rate should be kept high (10–13 ml min⁻¹). The effect of the hydrochloric acid flow rate on the sensitivity for As^{III} was observed to be negligible over the range 2–9 ml min⁻¹. The effect of hydrochloric acid

Fig. 2 Effect of reactor coil length (l_R) on the absorbance of 20 ng ml⁻¹ of As^{III}. Flow rate of water carrier, 9.2 ml min⁻¹. All other variables as in Table 1

Fig. 3 Effect of the flow rate of the water carrier on the absorbance of 20 ng ml⁻¹ of As^{III}. All other variables as in Table 1

Fig. 4 Effect of the concentration of HCl on the absorbance of 20 ng ml⁻¹ of As^{III}. Flow rate of HCl, 3.2 ml min⁻¹. A, Peak height absorbance; and B, relative standard deviation (%). All other variables as in Table 1

concentration on the arsenic signal response is shown in Fig. 4.

For the sodium tetrahydroborate stream, the sensitivity was constant between flow rates of 3.0 and 9.0 ml min⁻¹. The effect of sodium tetrahydroborate concentration on the arsenic signal response is shown in Fig. 5. An optimum of 1.0% m/v was chosen on the grounds of superior nickel interference tolerance at lower concentrations of sodium tetrahydroborate.³

The effect of the sample injection volume on the sensitivity of a 20 ng ml⁻¹ of As^{III} is shown in Fig. 6. Increasing the injection volume gave rise to an increase in sensitivity until the steady-state limit was reached at approximately 800 μ l. An injection volume of 409 μ l was chosen for all further work to optimize the throughput capability of the whole analysis system and obtain 75% of the steady-state absorbance signal.

The tolerance of the FI-HGAAS manifold to nickel interference was investigated without any matrix isolation. With prolonged processing of high nickel concentrations a slow deterioration in sensitivity was observed. Sensitivity was renewed by regular T-cell washing and conditioning with HF.^{17,25} The deterioration in sensitivity was attributed to the poisoning of the silica atomization cell surface by nickel salt, transported as a fine aerosol by the argon carrier gas to the T-cell, where it was deposited.³ Inclusion of a 0.25 μ m pore, 50 mm diameter PTFE membrane filter in-line with the hydride transport tubing eliminated this deterioration in sensitivity and removed the requirement for the

Fig. 5 Effect of the concentration of NaBH₄ solution on the absorbance of 20 ng ml⁻¹ of As^{III}. Flow rate of NaBH₄, 3.2 ml min⁻¹. A, Peak height absorbance; and B, relative standard deviation (%). All other variables as in Table 1

Fig. 6 Effect of sample injection volume on the absorbance of 20 ng ml⁻¹ of As^{III}. A, Peak height absorbance; and B, relative standard deviation (%). All other variables as in Table 1

Table 3 Effect of incorporating a membrane filter in-line between the gas-liquid separator and atomization cell on system performance. All other variables as in Table 1

Standard concentration/ ng ml ⁻¹ of As ^{III}	No membrane filter		Membrane filter	
	Absorbance	RSD (%)	Absorbance	RSD (%)
2.0	0.019	3.3 (n=10)	0.012	3.8 (n=12)
10.0	0.110	3.2 (n=10)	0.056	1.9 (n=12)
20.0	0.195	2.4 (n=6)	0.109	0.5 (n=12)

regular and tedious cell conditioning procedure. Inclusion of the PTFE membrane filter within the FI-HGAAS manifold reduced the sensitivity slightly but significantly improved precision, as shown in Table 3. The reduction in sensitivity may be explained by an increase in the gas-phase dilution of the generated hydride because of the increased volume of the gas transfer line. The improvement in precision observed was attributed to a slight increase in back-pressure within the gas-liquid separator and so damping pulsations in the argon carrier flow in addition to preventing droplets of reaction mixture reaching the T-cell.

The effect of both the concentration of the HCl reagent and the length of the reactor coil (l_R) on the nickel interference tolerance of the FI-HGAAS system is shown in Fig. 7. The interference-free determination (relative sensitivity $100 \pm 10\%$) of 20 ng ml^{-1} of As^{III} in the presence of up to $100 \text{ } \mu\text{g ml}^{-1}$ of nickel was achieved for the operating parameter values given in Table 1. By increasing the concentration of the hydrochloric acid reagent to 6.0 mol dm^{-3} and reducing the length of the reactor coil to 100 mm , the tolerance to interference was increased to a minimum of $200 \text{ } \mu\text{g ml}^{-1}$ of nickel. The decrease in sensitivity observed with these changes was not considered acceptable, however, and the initial variables (Table 1) were selected for subsequent analyses. An interference tolerance of $100 \text{ } \mu\text{g ml}^{-1}$ was considered more than sufficient, particularly with the use of matrix isolation prior to determination.

The tolerance of the system to interference was significantly higher than the $5 \text{ } \mu\text{g ml}^{-1}$ of nickel reported by Riby *et al.*¹⁵ A number of factors may be responsible for this. The $409 \text{ } \mu\text{l}$ injection volume in the present work introduces a smaller absolute amount of interferent than the $1000 \text{ } \mu\text{l}$ used by Riby *et al.* The concentrations of sodium tetrahydroborate in each system calculated after correction for dilution from other reagent streams are different; in the proposed manifold the concentration was $0.18\% \text{ m/v}$ in comparison with $0.38\% \text{ m/v}$ for the manifold of Riby *et al.* According to Welz and Schubert-Jacobs,³ a lower concen-

tration of sodium tetrahydroborate would be expected to give improved tolerance to interference. The order of addition of reagents is different. In the present system, the sample stream is merged first with hydrochloric acid and then with tetrahydroborate, whereas the opposite order was used by Riby *et al.*¹⁵ A comprehensive study of the effect, on both cation and anion interferences in the determination of arsenic and selenium, of the order of addition of tetrahydroborate and acid for a continuous-flow hydride generation system was made by Pierce and Brown.²⁷ They reported a substantial decrease in the extent of interferences when the acid was added before the tetrahydroborate but indicated that this order of addition of reagents gave a poorer precision. However, on applying a two-sided *F*-test ($P=0.05$) to the results presented by them,²⁷ the null hypothesis (that there is no significant difference between precisions) is retained. In a study of the continuous-flow determination of antimony and arsenic, Crock and Lichte²⁸ confirmed the effect of the order of addition of reagents on the extent of interference by cations. When tetrahydroborate is added first, some potentially interfering cations are reduced to the element or form borides or both. This consumes some of the tetrahydroborate reagent and provides a large surface area which can adsorb hydride-forming elements. When the tetrahydroborate is added after the acid, the formation of the gaseous hydrides is kinetically favoured.

Under the same experimental conditions (Table 1), 100 ng ml^{-1} of As^V could be determined without interference in the presence of up to $100 \text{ } \mu\text{g ml}^{-1}$ of nickel.

Optimization of the Continuous-flow Matrix Isolation Procedure

An investigation was made into the efficiency of the Dowex 50W-X8 cation-exchange resin incorporated into the continuous-flow matrix isolation unit against the variable of sample pH.

The relationship between the retention of nickel and sample pH at a sample flow rate 2.4 ml min^{-1} is shown in Fig. 8, from which it can be seen that the efficiency of the resin reached an optimum above pH 2.2. Breakthrough was judged to have occurred when the nickel concentration of the eluent exceeded $10 \text{ } \mu\text{g ml}^{-1}$ (10% of the maximum concentration of nickel that could be tolerated). The recovery of a 20 ng ml^{-1} As^{III} solution over the pH range 1.00–5.94 was quantitative (96.9–103.2%).

The design of the matrix isolation system has a number of beneficial features. Mounting the column of resin in the 'injection' loop of a six-port rotary valve allows intermittent regeneration of the column while the determination is proceeding in the hydride generation manifold or standards are being introduced for calibration purposes. The direction of acid regenerant flow is opposite to that used to load the column, hence, any tendency of the column contents to compact is minimized. As the resin is loaded in a continuous-flow mode, the dimensions of the resin are not critical. In a flow injection manifold, such dimensional changes could eventually lead to measurable changes in the dispersion coefficient.

Fig. 7 Effect of concentration of HCl reagent and length of reactor coil (l_R) on the interference of Ni in the determination of 20 ng ml^{-1} of As^{III}. A, [HCl] 3.6 mol dm^{-3} , l_R 600 mm ; B, [HCl] 7.2 mol dm^{-3} , l_R 600 mm ; and C, [HCl] 7.2 mol dm^{-3} , l_R 100 mm . All other variables as in Table 1

Fig. 8 A, Retention of Ni on the microcolumn as a function of sample solution pH; and B, recovery of As^{III} as a function of pH of sample solution. Sample flow rate, 2.4 ml min⁻¹

Optimization of the Stopped-flow KI Pre-reduction Procedure

For the determination of As^V using the operating parameter values given in Table 1 (no pre-reduction), the characteristic concentration was approximately 6.9 times larger than that for As^{III}. This may be attributed to the slower rate of hydride formation from solutions of As^V, for which a slow reduction to As^{III} must first occur.²³

Three separate sets of operating parameters were selected for which the ratio of the peak height for a 50 ng ml⁻¹ As^V standard solution relative to that of the same concentration of As^{III} was measured. The results are given in Table 4. For the values of the operating parameters used in investigation C, an average ratio of 96.7% (standard deviation 0.62% and 95% confidence interval $\pm 0.77\%$) was obtained for stop times between 5 and 30 s. Clearly this ratio is significantly different from 100%, suggesting that not all of the arsenic has been reduced. As the total concentration is known and the relative sensitivities for each oxidation state of arsenic are known, the percentage conversion of As^V to As^{III} may be calculated from the equation

$$S = x + R(100 - x)$$

where x is the percentage conversion, S is the ratio of the signals for the two forms of arsenic (expressed as a percentage of the As^{III} signal) and R is the sensitivity for As^V (expressed as a fraction of that of As^{III}). In this instance, $S = 96.7\%$ and R can be calculated from the relative characteristic concentrations (see earlier) to be 0.1449, from which it can be calculated that $x = 96.2\%$. The uncertainty in this number involves the uncertainty in R .

However, the nature of the calculation is such that the value of x is insensitive to fairly large variations in the value of R . For example, a variation of as much as $\pm 10\%$ in this ratio would only change the percentage conversion of As^V to As^{III} over the range 96.1–96.2%. It is arguable whether this conversion factor should be applied to all analyses regardless of the total arsenic concentration, as it might be expected that for lower concentrations a higher degree of conversion would be obtained during the stop time (and *vice versa*). This assumes that the rate of conversion is related to the ratio of the concentration of iodide to that of arsenic. It would be desirable to avoid such considerations and any future studies of this procedure should be directed towards achieving a percentage conversion indistinguishable from 100%. Such an investigation might consider other reducing agents and the use of on-line heating.²⁹

The same arguments apply to the benefits of the design of the pre-reduction manifold with a flow injection valve interface, as have been proposed for the decoupling of the matrix isolation procedure and the hydride generation chemistry. The conditions for efficient pre-reduction may be optimized separately from those of the hydride generation reaction. The stopped-flow format allows reagents used in the pre-reduction chemistry to be conserved. This is particularly important with potassium iodide, which is used in high concentration. It also allows the reaction time to be controlled independently of any other parameter such as flow rate or tube length. For example, if the combined flow rates of sample and reagents were 5.8 ml min⁻¹, to achieve a residence time of 20 s would require an additional 3.8 m of 0.8 mm i.d. tubing. A minimum amount of pre-reduction reagent is introduced into the hydride generation manifold and thus reagents which give unpleasant reduction products (such as hydrogen sulfide) with tetrahydroborate could possibly be tolerated. This extends the range of reagents available for investigation as pre-reductants. The reagents dilute only the sample solution and, unlike the situation in which the pre-reduction is performed in the hydride generation manifold,^{12,13} do not contribute to the on-line dilution of the acid and tetrahydroborate.

Analysis of Nickel-based Alloy BCS-346

In order to validate the matrix isolation system, the analysis of a nickel-based alloy (BCS-346) was attempted. Riby *et al.*¹⁵ reported a microwave digestion procedure for this material with subsequent determination of the arsenic content against As^{III} standards prepared in-house from sodium arsenite. As accurate results were obtained, it would seem that the digestion procedure did not oxidize the arsenic to the +5 state. It was found that with the digestion method described previously¹⁵ it was necessary to use six

Table 4 Effect of manifold variables on the performance of the stopped-flow KI pre-reduction system for the reduction of 50 ng ml⁻¹ of As^V. A: Sample, 2.2 ml min⁻¹; KI, 1.4 ml min⁻¹ (20% m/v); HCl, 1.5 ml min⁻¹ (12 mol dm⁻³). B: Sample, 2.2 ml min⁻¹; KI, 1.4 ml min⁻¹ (30% m/v), HCl, 1.5 ml min⁻¹ (12 mol dm⁻³). C: Sample, 2.2 ml min⁻¹; KI, 1.4 ml min⁻¹ (30% m/v); HCl, 2.2 ml min⁻¹ (12 mol dm⁻³)

Stop time/s	Peak height relative sensitivity* (%)		
	Investigation A	Investigation B	Investigation C
5	—	79.9	97.5
10	77.6	86.6	95.2
15	82.3	90.4	97.5
20	80.4	97.0	96.7
30	89.2	95.6	96.7
45	92.1	95.6	—
60	94.8	95.5	—

* As^V with respect to As^{III}.

digestion vessels, containing either samples or acid blanks, in the programme to prevent venting and therefore analyte loss.

Initially, the determination of arsenic in a synthetic nickel matrix (25 ng ml⁻¹ of As^{III}, 500 µg ml⁻¹ of Ni), following microwave digestion, was attempted using the continuous-flow matrix isolation FI-HGAAS system but without iodide pre-reduction. The results showed an arsenic recovery, relative to As^{III} standard solutions, of 11.4%, indicating either loss of analyte, oxidation of arsenic to the +5 oxidation state during digestion or interference from the nickel matrix. Two 25 ng ml⁻¹, As^{III} standard solutions (no nickel added) were subsequently taken through the same digestion procedure, after which they were analysed as before, both directly and after a manual iodide pre-reduction procedure⁶ had been applied. The recoveries obtained for the two sets of analyses were 14.7 and 14.7, and 102.9 and 101.5%, respectively. It was concluded that the microwave digestion procedure converted the arsenic present within the sample to the +5 oxidation state.

Analysis was therefore subsequently performed with the pre-reduction procedure and continuous-flow matrix isolation as already described. The analysis was carried out within 24 h of sample digestion because after this the sample solution was observed to contain a significant amount of precipitated material. The system was calibrated using aqueous standards (0–80 ng ml⁻¹ of As^{III}). Calibration was linear up to at least 80 ng ml⁻¹ of As^{III}, having a slope of 2.06×10^{-3} absorbance ng⁻¹ ml, an intercept of 8.3×10^{-3} absorbance and a correlation coefficient of 0.9993. The precision of the system based on the measurement of the concentration in the digested nickel alloy sample was 1.0% (relative standard deviation) for six replicate injections.

It is considered that the true precision of the over-all method for this determination would be worse than this value as it does not take into account the uncertainty due to the calibration procedure and the extent of the reduction by iodide. Measurement of the true over-all precision would be a very time-consuming and costly procedure, as a large number of replicate determinations would need to be made, each using a separate portion of the solid standard reference material and a fresh calibration data set prepared from new calibration solutions prepared, in turn, from a new stock standard solution. In practice, such an evaluation of an analytical procedure is hardly ever attempted. This still leaves the real problem of how to obtain a reliable estimate of the over-all precision as this is needed to evaluate the accuracy of the method. Evaluation of the accuracy requires that the hypothesis, that there is no significant difference between the analytical result and the certified value, be tested. The significance test usually employed for this purpose is the *t*-test. However, this test requires a know

ledge of the standard deviations of the two mean values to be compared and a knowledge of the number of replicates from which the two means were calculated. Often this information is not available for the standard reference material, under which circumstances there are two possible outcomes of the attempt to validate a method. Either a result obtained by the new method falls within whatever uncertainty the certifying agency provides, in which event the result may be deemed 'accurate', or the result obtained does not fall within this uncertainty interval. The question then arises of how to make an evaluation of the accuracy of the procedure under investigation when this latter situation occurs. This problem, which, from a study of the original literature concerning trace element determinations, must often occur, is not covered by the standard texts on statistical procedures for analytical chemists.

The following protocol is suggested. Estimates of the 95% confidence intervals about the two values to be compared are made and, if these intervals touch or overlap, no significant difference in the values is indicated and the method may be considered accurate. It is recognized that such an overlap may occur because the uncertainty in the proposed method may be very large. In these circumstances some professional judgment is called for, as, although the method may pass the test for being accurate, it may have such poor precision as to be useless in practice. This scenario is, of course, possible even when all the data for a proper application of the *t*-test are available.

An estimate of the 95% confidence interval for the reference material may be made as the certificate gives four results from different analysts for the arsenic content of BCS-346, namely 50.0, 51.8, 52.0 and 47.0 µg g⁻¹. It may be readily calculated that the mean, standard deviation and 95% confidence interval of these values are 50.2, 2.3 and ± 3.7 µg g⁻¹, respectively. These last two values underestimate the true uncertainty as each individual result is subject to some uncertainty. No information as to the likely magnitude of the uncertainty in any individual analyst's value is given, other than the use of three (presumably) significant figures.

Calculation of the confidence interval for the measured result is not straightforward. Some assumptions need to be made; these include the consideration that the major sources of uncertainty in the procedure are the error introduced by the calibration and the extent of the reduction of As^V to As^{III}. A typical calibration data set is given in Table 5. An unweighted least-squares regression analysis of these data produced the results also given in Table 5. The standard deviations of the two results are 0.89 and 0.88 ng ml⁻¹ for solution concentrations of 47.1 and 46.4 ng ml⁻¹, respectively.³⁰ The corresponding 95% confidence intervals are both ± 2.46 ng ml⁻¹. The concentrations

Table 5 Calibration data and analysis of BCS-346

Sample mass/g	Standard concentration/ng ml ⁻¹	Absorbance	Mean absorbance	Corrected absorbance*
	0.0	0.006, 0.006, 0.007	0.006 ₃	
	10.0	0.028, 0.029, 0.029	0.028 ₇	
	20.0	0.051, 0.051, 0.052	0.051 ₃	
	40.0	0.095, 0.093, 0.093	0.093 ₇	
	60.0	0.132, 0.133, 0.132	0.132 ₃	
	80.0	0.170, 0.170, 0.170	0.170 ₀	
1.0399		0.103, 0.101, 0.101	0.101 ₁	0.105 ₁
1.0334		0.101, 0.100, 0.100	0.100 ₃	0.103 ₇

Regression equation: $y = 0.00204_6x + 0.00877_3$, $s_{y/x} = 2.50_6 \times 10^{-3}$, $s_b = 3.63_6 \times 10^{-5}$, $s_a = 1.63_3 \times 10^{-3}$, where *y* is absorbance, *x* is concentration (ng ml⁻¹), $s_{y/x}$ is the standard deviation of the *y*-residuals, s_b is the standard deviation of the slope and s_a is the standard deviation of the intercept.³⁰

* The corrected absorbance values are those which would have been obtained had all the arsenic in the sample been reduced to As^{III}.

Table 6 Result of the analysis of BCS-346 nickel alloy reference material

Sample No.	As found/ $\mu\text{g g}^{-1}$ *	Certified value for As/ $\mu\text{g g}^{-1}$ *
1	45.3 ± 2.37	50.2 ± 3.7
2	44.9 ± 2.38	—

*The $\pm$ terms are 95% confidence intervals.

in the solid samples are therefore 45.3 and $44.9 \mu\text{g g}^{-1}$ with confidence intervals ± 2.37 and $\pm 2.38 \mu\text{g g}^{-1}$, respectively. Thus, even without a consideration of the uncertainty due to the percentage reduction of As^{V} to As^{III} , the 95% confidence intervals of the measured value and for the certified value overlap. The results are summarized in Table 6.

A characteristic concentration (0.0044 absorbance) of 2.1 ng ml^{-1} of arsenic was obtained. A detection limit of 3.9 ng ml^{-1} of arsenic was calculated from the resultant calibration graph.³⁰ A sample throughput of 18 h^{-1} was achieved with triplicate injections.

Conclusion

The FI-HGAAS manifold with continuous-flow matrix isolation was successfully used for the determination of arsenic in a nickel-based alloy, after modification to include a stopped-flow iodide pre-reduction procedure. The same stopped-flow pre-reduction procedure could also be applied prior to the determination of other hydride-forming elements such as antimony.²⁰ Full automation of the system, including the stopped-flow pre-reduction procedure, should be possible with existing apparatus.³¹

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