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Elimination of Copper Interference by Continuous Flow Matrix Isolation in the Determination of Selenium by Flow Injection Hydride Generation Atomic Absorption Spectrometry*

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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 copper interference in the determination of selenium by flow injection hydride generation atomic absorption spectrometry. The microcolumn manifold used for the selective retention of the copper interferent was interfaced with the hydride generation manifold through a flow injection sample injection valve. The two manifolds were made independent of each other in order to achieve optimum performance characteristics for both the matrix isolation and hydride generation. Following removal of the copper, a 400 µl sample was injected into a water carrier stream. This was merged with hydrochloric acid and subsequently with sodium tetrahydroborate soution. After introduction of argon, the selenium hydride was separated by a glass U-tube separator and atomized by a tube-in-flame atomizer. The intermittent regeneration of the column with 1 mol dm^{-3} HCl enabled repeated matrix isolation without any loss in resin efficiency or the need for column repacking and gives the option for total automation. The procedure was validated through accurate analyses of two copper metal reference materials, National Institute of Standards and Technology Standard Reference Material 454 Unalloyed Copper XI and Bundesanstalt für Materialforschung und -prüfung, Germany, Certified Reference Material 361 Copper, containing 479 and 36 µg g^{-1} of Se^{IV}, respectively. The system was found to have a characteristic concentration of 1.0 ng ml^{-1}, limit of detection of 2.1 ng ml^{-1}, relative standard deviation of 1.5% (10 ng ml^{-1} Se^{IV}, n = 12) and sample throughput of 51 h^{-1}.

Keywords: Selenium determination; flow injection hydride generation atomic absorption spectrometry; copper interference removal; continuous flow matrix isolation

Copper has been cited as a serious interfering element in the determination of selenium by hydride generation atomic absorption spectrometry (AAS).[1-5] Many attempts have been made to remove or reduce this interference with varying degrees of success. Interference reduction has been reported through the optimization of both acid and sodium tetrahydroborate concentrations,[3,4] and the application of a variety of complexing agents.[6-11]

Various manual matrix isolation procedures have been applied to hydride generation AAS including coprecipitation[12] and ion exchange[13-16] but they have the disadvantage of being tedious, labour intensive and to some extent dependent on operator skill. A variety of resins have been used for matrix isolation including, Chelex 100,[13-16] Dianion SK1B[15] and Dowex 50W-X16.[16] Hershey and Keliher[16] successfully applied Dowex 50W-X16 cation-exchange resin for the isolation of both arsenic and selenium from a wide range of interfering matrix species including Cu, Ni, Co and Ag. The resin was reported to be more beneficial than the Chelex 100 resin especially when dealing with environmental samples, as the Chelex 100 resin gave poor analyte recovery for some samples.

With the introduction of continuous flow hydride generation to replace discrete batch methods, a reduction in interference has been reported.[14,17] A further development in continuous flow methodology, that of the use of the flow injection (FI) format, was first reported by Åström.[18] The use of FI techniques has been reported for the determination of hydride-forming elements giving accuracy, precision, low sample and

reagent consumption and superior sample throughput capabilities in comparison with both continuous flow and discrete batch methods.[18-26] Flow injection hydride generation AAS has been reported to reduce interference effects, including that of copper, in the determination of selenium.[19,20,23]

A variety of procedures for the automation of sample pre-treatment in AAS have developed with FI methodology. Systems capable of both pre concentration and matrix isolation employing liquid–liquid extraction,[27,28] ion exchange[29,30] and precipitation[31,32] have been reported.

To date, little attempt has been made to apply such systems to the removal of interference effects in hydride generation AAS. Ikeda[33] reported a system incorporating a microcolumn of chelating resin, for the removal of copper and nickel in the determination of selenium. Although matrix isolation was carried out on-line, the system relied on manual sample pipetting, had limited precision and no facility for column regeneration.

Riby et al.[34] have recently reported on a system for the determination of arsenic in a nickel-based alloy by using continuous flow hydride generation AAS, incorporating on-line matrix removal via a microcolumn of strong cation-exchange material (SCX). Although successful for the application, some degree of compromise had to be made between the performance characteristics of the matrix isolation system and the hydride generation manifold itself. Column regeneration was carried out after every four determinations by pumping 1 mol dm^{-3} HCl through the column to waste, after disconnecting the sample line.

This paper reports an FI system for the determination of selenium by hydride generation AAS. Elimination of the interference from copper is achieved by a continuous flow matrix
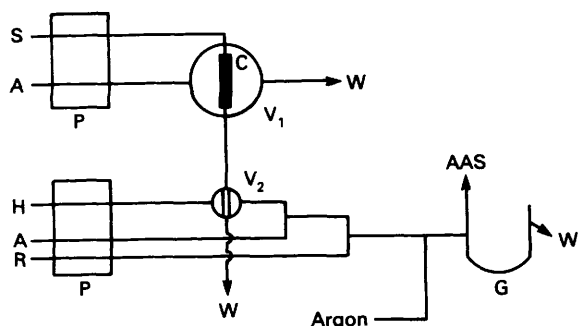
Fig. 1 Schematic diagram of the FI manifold with a continuous flow matrix isolation unit: P, peristaltic pump; S, sample; H, water; A, HCl; R, $NaBH_4$; W, waste; V_1, switching valve; V_2, sample-injection valve; C, microcolumn; and G, gas–liquid separator

isolation procedure based on a microcolumn of strongly acidic cation-exchange resin (Dowex 50W). The manifold design lends itself to full automation and overcomes the limitations of previously reported systems.[33,34]

Experimental

Apparatus

A Philips Scientific SP9 atomic absorption spectrometer equipped with a Philips data coded selenium hollow cathode lamp, operated at 7.5 mA was used for all determinations. A spectral bandpass of 1.0 nm was used with the 196.0 nm selenium spectral line. The signals were recorded on a Tekman TE 200 chart recorder (2–10 mV range), all measurements being expressed as peak-height absorbance. A 50 mm Philips Scientific universal burner was used to support the air–acetylene flame-heated T-shaped silica cell (air flow setting, 28; acetylene flow setting, 15). The FI hydride generation manifold shown in Fig. 1 was developed from the gas–liquid separator and hydride atomization systems of a Philips Scientific PU9360 continuous flow vapour system. Two peristaltic pumps were employed. A Gilson Minipuls 3 was used for the hydride generation manifold and a Gilson Minipuls 2 for the matrix isolation unit. Control of the flow-rates was achieved through application of different bore standard manifold tubing (Altec). All manifold tubing consisted of 0.8 mm i.d. polytetrafluoroethylene (PTFE) tubing (Anachem). Manifold channels were connected through three-way connector T-pieces (Anachem), which aided reagent mixing. A micro-bore glass column [50 × 3.0 mm i.d. (Anachem)] fitted with porous 25 μm PTFE frits was incorporated into the external sample loop of a rotary sample injection valve (Anachem). Sample injection was acheived using a Rheodyne Model 5020 fixed volume loop injector valve operated by an electrically activated universal valve switching unit (Anachem). Sample loops of various volumes were prepared using PTFE tubing (0.5–1.5 mm i.d.) cut to appropriate lengths.

Reagents

Analytical-reagent grade water produced by a LiquiPure RG system (reverse osmosis followed by ion exchange), was used for all solutions and as a carrier stream. A sodium tetrahydroborate solution (1% m/v in a 0.1% m/v NaOH solution) was prepared using sodium tetrahydroborate pellets (SpectrosoL, BDH) and filtered through a Whatman 541 filter-paper. With refrigeration, this solution was usable for up to 3 d. The hydrochloric acid (6 mol dm⁻³) reagent solution was of SpectrosoL grade (BDH). All selenium(IV) standard solutions were prepared by dilution of a standard solution of selenous acid (SpectrosoL, BDH) containing 1000 μg ml⁻¹ of Se^IV. For the interference investigation work copper(II) sulphate pentahy-

Table 1 Optimized variables for hydride generation AAS with continuous flow matrix isolation. Injection volume, 409 μl

Hydride generation AAS—

Reagent	Concentration	Flow-rate/ml min⁻¹
H_2O carrier	—	6.0
HCl	6 mol dm⁻³	4.2
$NaBH_4$	1.0% m/v	3.2
Ar	—	600

Continuous flow matrix isolation—

Reagent	Concentration	Flow-rate/ml min⁻¹
Sample	<1000 μg ml⁻¹ Cu	2.0
HCl (column regenerant)	1.2 mol dm⁻³	2.0

drate (AnalaR, BDH) was used to prepare interferent standards. Conditioning of the T-shaped silica atomization cell was carried out using a 5% v/v solution of hydrofluoric acid (AnalaR, BDH). High-purity argon was used as the purge gas (99.998% Ar, BOC). The digestion of the copper metal reference materials was carried out using nitric acid (Aristar, BDH) and hydrochloric acid (Aristar, BDH). The cation-exchange resin was Dowex 50W-X8 (Drymesh 100–200, hydrogen form, 8% cross linkage, Sigma). Two copper metal reference materials, National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 454 Unalloyed Copper XI and Bundesanstalt für Materialforschung und -prüfung (BAM) Certified Reference Material (CRM) 361 Copper, were obtained from the Bureau of Analysed Samples (Middlesbrough, UK). The microcolumn was packed under suction with an aqueous slurry of Dowex 50W-X8–200 resin (250 mg of dry resin).

Study of Operational Variables

Operating conditions for analysis procedure

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 2.0 ml min⁻¹.

The hydride-generation manifold and matrix-isolation unit were operated according to the optimized variables shown in Table 1. The optimized variables were obtained using the same optimization procedure as Riby et al.[34] In obtaining the optimum variables, sensitivity was a prime concern but consideration was also given to precision, interference tolerance and reliability of the system. A more rigorous approach to optimization could have been carried out but it was decided that it was not necessary to prove the benefits of the manifold design. Standard solutions, requiring no matrix isolation, were pumped continuously through the injection valve, bypassing the microcolumn. The injection valve was activated intermittently (load time, 20 s; and injection time, 10 s) thereby sampling the standard solution and introducing it into the hydride-generation manifold.

Following the introduction of the standards the microcolumn was switched into the sample line and analytical-reagent grade water was continuously pumped through it to remove the hydrochloric acid.

After washing the column, the sample was also introduced by continuous pumping. In order to fill the void volume of the column and pump tubing, the sample was pumped continuously for 60 s prior to sampling of the column eluent, as described for standard solutions. After triplicate injections, the microcolumn was regenerated (using HCl) and the sample line washed with analytical-reagent grade water. [Hydrochloric acid (1.2 mol dm⁻³) was pumped continuously through the microcolumn in the opposite direction to that of the sample flow (2 ml min⁻¹, 30 s).] Following the short period of regeneration, the column was switched back in-line and the sampling procedure re-

Table 2 Summary of the sampling procedure for matrix isolation, including timing sequences

Timing sequence (t)/s	Operation
0	V_S*, H_2O pumped *via* column
20	V_S, sample pumped *via* column
80	V_I†, activation (load position)
100	V_I, activation (inject position)
110	V_I, activation (load position), injection procedure repeated to give triplicate injections
170	V_B‡, HCl regenerant pumped *via* column, H_2O pumped *via* sample line
200	V_S, H_2O pumped *via* 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.

peated. During the transference of the sample uptake tube from sample to analytical-reagent grade water, the sample pump was stopped in order to prevent the introduction of air into the column. The hydride-generation manifold was employed continuously throughout the whole procedure, independently of the matrix-isolation unit. A summary of the sampling procedure including timing sequences is shown in Table 2.

Digestion procedure

The method[33] used for the digestion of the two copper metal reference materials, NIST SRM 454 and BAM 361 was as follows.

A sample of copper metal (0.5 g) was accurately weighed into a clean Pyrex beaker (50–100 ml). To the beaker were added 10 ml of 8 mol dm^{-3} HNO_3 and the beaker was covered with a watch-glass. The beaker was placed on a hotplate, and the contents were heated to near dryness, then removed from the hotplate. Once cool, 10 ml of 6 mol dm^{-3} HCl were added and the beaker was placed in a steam-bath. After approximately 15 min of heating, in order to dissolve the sample residue, the resultant solution was allowed to cool. The cool digest solution was transferred into a calibrated flask (100 ml) and diluted to volume with analytical-reagent grade water. Prior to analysis, the NIST SRM 454 and BAM 361 digests were further diluted to produce working samples containing 75 and 1000 µg ml^{-1} of copper, respectively.

Results and Discussion

Optimization of FI Hydride-generation Method

The effect of the argon carrier gas flow-rate over the range 200–600 ml min^{-1} was studied. Increasing the argon flow-rate caused a significant increase in peak-height absorbance and rate of transport of the hydride to the atomization cell.

The performance of the manifold was significantly affected by the condition of the silica atomization T-cell. Performance characteristics varied from one cell to another, depending on age and analytical history. Previously unused T-cells showed very poor performance characteristics. This problem was overcome to some extent by conditioning the surface of the silica cell.[35] The silica cells were soaked in a solution of hydrofluoric acid (5% v/v) for a period of 4 h in order to etch the surface and therefore aid hydride atomization. For the new silica cells in particular, an improvement in performance was observed with repeated use and after processing relatively high concentrations of hydride. At the start of each analysis, a standard solution of 1000 ng ml^{-1} of Se^{IV} was injected two or three times. This procedure enhanced both the precision and sensitivity of the system for all subsequent determinations.
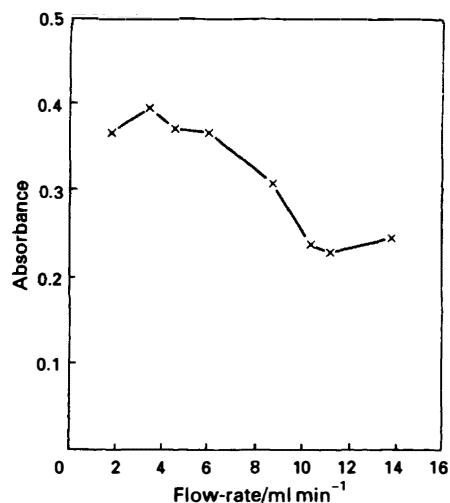

Fig. 2 Effect of the flow-rate of $NaBH_4$ solution on the absorbance of 100 ng ml^{-1} of Se^{IV}. Concentration of $NaBH_4$, 1.0% m/v; concentration of HCl, 3.6 mol dm^{-3}. All other variables as in Table 1
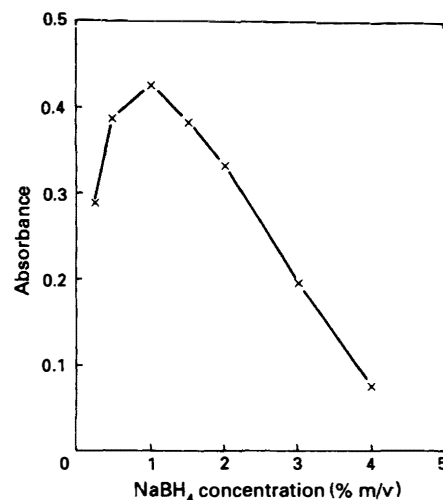

Fig. 3 Effect of the concentration of $NaBH_4$ solution on the absorbance of 100 ng ml^{-1} of Se^{IV}. Flow-rate of $NaBH_4$, 3.2 ml min^{-1}; concentration of HCl, 3.6 mol dm^{-3}. All other variables as in Table 1

The effect of the hydrochloric acid flow-rate on the sensitivity for Se^{IV} was observed to be negligible over the range 2–14 ml min^{-1}. This observation was unexpected and to some extent unexplained. The increase in the hydrochloric acid flow-rate, which was predicted to reduce signal response by dilution, appears to be offset by an increased rate of transport through the gas–liquid separator. The hydrochloric acid concentration was also observed to have little or no effect on the selenium signal response over the range of 1.2–7.2 mol dm^{-3}. The optimum hydrochloric acid concentration was decided after consideration of the tolerance of the system to the copper interference, which is reported later.

Both the flow-rate and concentration of sodium tetrahydroborate were observed to have a significant effect on the sensitivity of the system as shown in Figs. 2 and 3, respectively.

The relationship between the flow-rate of the aqueous carrier solution and the resulting peak-height absorbance is shown in Fig. 4. It can be seen that to achieve maximum sensitivity, the carrier flow-rate should be kept as high as possible. The optimum carrier flow-rate was decided upon after consideration of the tolerance of the system to copper interference, which is reported later.

The effect of the sample injection volume on the sensitivity of Se^{IV} is shown in Fig. 5. Increasing the injection volume gave rise to an increase in sensitivity until the steady-state limit was reached at approximately 700 µl. Although high in-
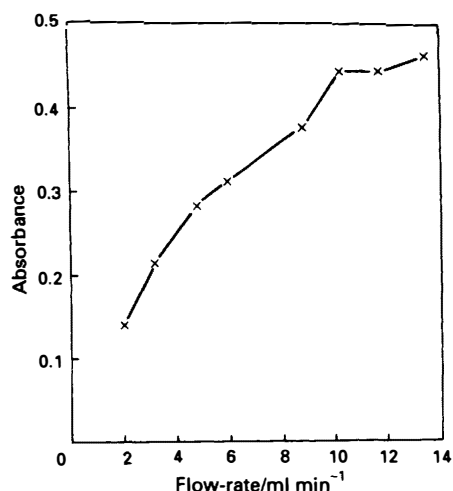
Fig. 4 Effect of the flow-rate of the water carrier on the absorbance of 100 ng ml^{-1} of Se^{IV}. Concentration of HCl, 3.6 mol dm^{-3}. All other variables as in Table 1
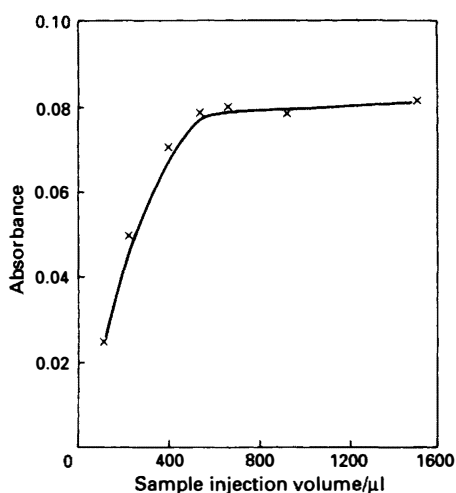

Fig. 5 Effect of the sample injection volume on the absorbance of 20 ng ml^{-1} of Se^{IV}. Concentration of HCl, 3.6 mol dm^{-3}. All other variables as in Table 1

Table 3 Manifold performance data for determination of selenium

H$_2$O carrier flow-rate/ ml min^{-1}	Injection volume/ µl	Characteristic concentration/ ng ml^{-1}	RSD* (%)
6.2	409.3	0.96 (0.39)†	1.3
13.0	409.3	0.79 (0.32)†	1.5
13.0	922.3	0.50 (0.46)†	1.6

* Relative standard deviation (*n*=9).
† Characteristic concentration in absolute terms (ng of Se^{IV}).

jection volumes favoured high sensitivity, reducing the injection volume reduced the sample volume requirement and improved the throughput. An injection volume of 409 µl was used for all further investigative work and this volume produced 90% of the steady state absorbance signal. Performance data for combinations of aqueous carrier flow-rate and injection volume are given in Table 3.

Prior to the investigation into matrix isolation, a study was made of the tolerance of the hydride-generation manifold to copper interference. In agreement with the work of Welz and Melcher[3] and Welz and Schubert-Jacobs,[4] the tolerance could be significantly improved by employing high hydrochloric acid concentrations as shown in Fig. 6. An optimum hydrochloric acid concentration of 6.0 mol dm^{-3} was chosen for the analysis after consideration of the interference tolerance, the
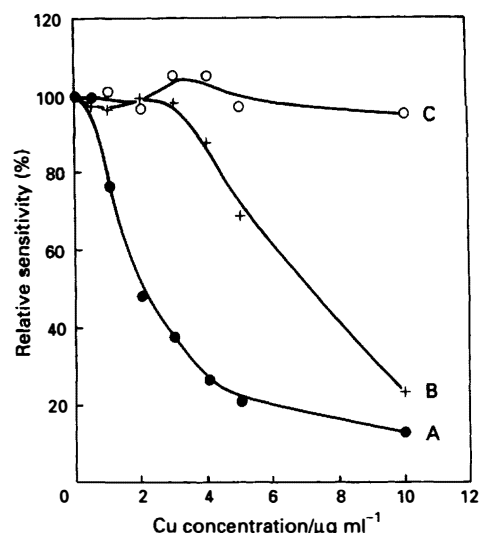

Fig. 6 Influence of the HCl concentration on the interference of Cu in the determination of 20 ng ml^{-1} of Se^{IV}: A, 2.4; B, 6.0; and C, 9.6 mol dm^{-3} HCl. All other variables as in Table 1

hydrochloric acid consumption and the difficulty in pumping high concentration acids.[33] The water carrier flow-rate was kept at 6.0 ml min^{-1}, in order to reduce the dilution of hydrochloric acid in the hydride-generation system and to optimize the precision, whilst retaining an adequate sensitivity during the proposed analyses. Because of the manifold design, the injected sample was merged with the hydrochloric acid reagent prior to the sodium tetrahydroborate solution. This order of reagent addition was the reverse of that reported in other systems.[33,34] The hydrochloric acid was added prior to the sodium tetrahydroborate solution in order to reduce the time interval between the addition of the reductant and the hydride separation in which the reduction of the interferent could occur. Controlling the reaction time in such a manner as to favour the main hydride-generation reaction enhances interference tolerance, as reported by Åström.[18]

Optimization of the Continuous Flow Matrix Isolation Procedure

The Dowex 50W cation-exchange resin was chosen for use in this work because it has been previously reported to be applicable to matrix isolation in hydride-generation AAS.[16]

An investigation was made into the efficiency of the resin, incorporated into the continuous flow matrix isolation unit, against the variables of sample flow-rate and sample pH. The copper capacity of the column was assessed for the two variables, by pumping a 1000 µg ml^{-1} copper standard solution through the column and continuously monitoring the copper concentration of the column eluent by flame atomic absorption spectrometry (FAAS). Breakthrough of the column was judged to have occurred when the copper concentration of the column eluent exceeded 1.0 µg ml^{-1}. The efficiency of the resin improved with reduced sample flow-rate (sample pH 4.0) owing to increased contact time between the copper ions and the active sites of the resin (Fig. 7).

Interfacing the matrix-isolation manifold and the hydride-generation manifold with a sample injection valve, as reported by Nord and Karlberg[28] for liquid–liquid extraction with FAAS, proved extremely beneficial to the systems performance. As the matrix-isolation unit was independent of the hydride-generation manifold, the sample flow-rate through the column could be kept low in order to keep the column efficiency high, without having to compromise the sensitivity of the hydride-generation manifold, as reported for the system of Riby *et al.*[34] in which the microcolumn was situated on-line. By pumping the sample at low flow-rates, prob-
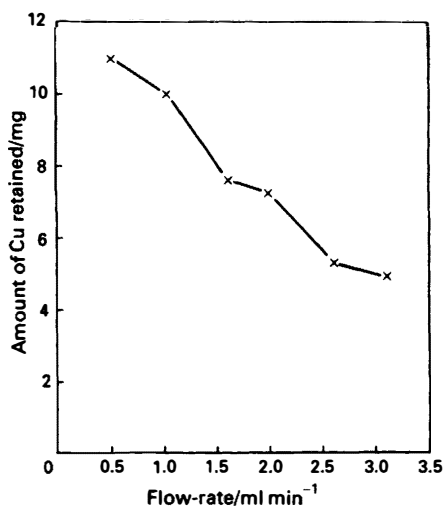
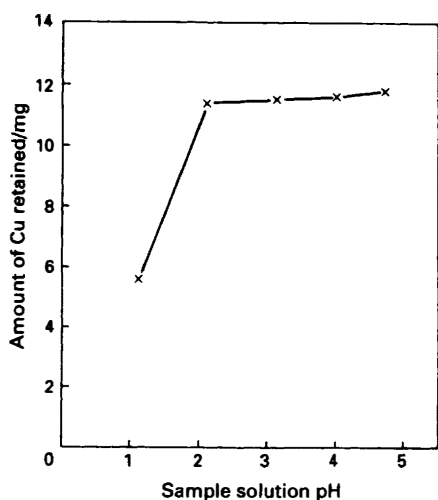**Fig. 7** Retention of Cu as a function of sample flow-rate through the microcolumn. Sample solution pH, 4.0

Fig. 8 Retention of Cu on the microcolumn as a function of sample solution pH. Sample flow-rate, 2.0 ml min^{-1}

lems with resin compaction in the column and build-up of high back-pressures were eliminated. On the introduction of copper (1000 µg ml^{-1}) to the column resin, high concentrations of hydrogen ions were eluted from the resin by the process of cation exchange. The drop in pH, associated with this exchange process, produced a slight shrinkage of the resin but this caused no detrimental effect to the system as the shrinkage was reversed on regeneration of the resin. A sample flow-rate of 2.0 ml min^{-1} through the column was decided upon after consideration of both the column efficiency and sampling rate. At a sample flow-rate of 2.0 ml min^{-1}, the 409 µl sample loop of the injection valve could be filled in 20 s.

As shown in Fig. 8 from the relationship between the retention of copper and the sample pH (sample flow-rate 2.0 ml min^{-1}), the efficiency of the resin reached an optimum above pH 2.0. The retention of copper, at pH values above 5.0, was not investigated because the addition of ammonia solution, in order to obtain such pH values, caused turbidity of the samples. Such turbidity was assessed to be a source of analyte loss through coprecipitation.[16]

The incorporation of the microcolumn within the sample loop of an injection valve permitted the intermittent regeneration of the column without the need to dismantle the hydride-generation manifold or replace the column, as reported for previous systems.[33,34] By directing the regenerant solution to flow in the reverse direction to that of the sample, the possibility of column resin compaction was

eliminated. During the regeneration procedure, water was pumped through the sample line and injection valve to waste, in order to wash out the previous sample. During the column regeneration process, it was possible to analyse standard solutions, which bypassed the column, to check for sensitivity drift. After 3 months of continued use and regeneration, the performance of the matrix-isolation column was similar to that obtained when the column was initially packed with resin.

Analysis of Copper Metal Reference Materials NIST SRM 454 and BAM 361

In order to validate the matrix isolation system, analyses of two copper reference materials, NIST SRM 454 Unalloyed Copper and BAM 361 Copper, was attempted.

Prior to analysis, the metal digest solutions were adjusted to pH 4.00 with the addition of ammonia solution. This produced some degree of precipitation and significantly reduced the capacity of the column. The reduction in capacity was identified as owing to a competition between copper and ammonium ions for the active sites on the resin. In order to overcome this problem, the pH adjustment step was removed from the sample preparation. The pH values of the two analysed samples NIST SRM 454 and BAM 361 were 2.1 and 1.1, respectively, therefore even without pH adjustment the column capacity was still sufficient to permit triplicate injections of each sample solution before column regeneration (column capacity >5.0 mg of copper). The removal of the pH adjustment step had the further advantage of reducing: (*i*) sample preparation time; (*ii*) the chance of sample contamination; and (*iii*) the chance of precipitation. Thus the loss of analyte through coprecipitation[16] was eliminated.

The results of the analyses of the reference materials are given in Table 4. The system was calibrated using aqueous standards (5–50 ng ml^{-1}). Calibration was linear up to at least 50 ng ml^{-1} of Se^{IV} having a slope of 4.35 × 10^{-3} A ng^{-1} ml, an intercept of 5.1 × 10^{-3} A and a correlation coefficient of 0.9992.

The precision of the system, based on injections of an aqueous 10 ng ml^{-1} Se^{IV} standard, was 1.5% relative standard deviation (RSD), ($n = 12$). A characteristic concentration of 1.0 ng ml^{-1} Se^{IV} was routinely achieved. The detection limit of 2.1 ng ml^{-1} was calculated from the resultant calibration graph.[36] A sample throughput of 17 h^{-1} was achieved with triplicate injections.

The sensitivity of the system compared well with that of the conventional operation of the Philips PU9360 continuous flow vapour system. For steady-state analysis (sample volume, 5.0 ml) a characteristic concentration of 0.91 ng ml^{-1} Se^{IV} was reported.[37] For less difficult samples, the characteristic concentration could be improved by increasing the carrier flow-rate and injection volume (see Table 3).

One of the major advantages of this system design, in comparison with others, is the high precision obtained. For the system of Riby *et al.*[34] and Ikeda[33] the RSDs quoted for the determinations of 10 ng ml^{-1} of As^{III} and 10 ng ml^{-1} of Se^{IV} were 3.0 and 3.8%, respectively. These figures are clearly inferior to those quoted in this work. Such poor precision can be attributed to crude sample introduction procedures into the two manifolds. In the system of Ikeda[33] a 500 µl sample was introduced manually from a Pipetman P-1000. Riby *et al.*[34] employed a timed injection procedure, pumping the sample

Table 4 Results of analyses of copper metal reference materials (±95% confidence interval)

Sample	Certified value for Se^{IV}/ µg g^{-1}	Se^{IV} found/ µg g^{-1}
NIST SRM 454	479 ± 8	476.0 ± 7.2
BAM 361	36 ± 0.6	37.1 ± 0.7

continuously into the system over a short period of time (10 s). The timing was carried out manually, using a Seiko analogue stop watch, which would make the precision very susceptible to operator performance and slight fluctuations in the flow-rate.

In the system of Riby et al.,[34] the incorporation of the matrix isolation on-line required a compromise in the performance characteristics for the matrix isolation and hydride generation. Optimum sensitivity was achieved at a carrier flow-rate of 9.0 ml min⁻¹ and yet the optimum matrix isolation characteristics were achieved at 2–4 ml min⁻¹. Even at a compromise of 6.0 ml min⁻¹, the system was susceptible to high back-pressure and column compaction problems, requiring intermittent replacement of the column. In the proposed system, no problem with back-pressure or column compaction was observed, as the sample flow-rate through the column was kept low (2.0 ml min⁻¹) thereby optimizing matrix isolation, without compromising the hydride-generation performance.

By incorporating the matrix-isolation column within the sample loop of an injection valve, the rapid intermittent regeneration of the column took place without interrupting the operation of the hydride-generation manifold. Ikeda[33] reported no column regeneration facility in the system used. The column was simply replaced after every 25 determinations (column capacity, 50 mg of Cu). By employing a relatively large column, in order to increase the column capacity, the sample throughput was restricted to 30 h⁻¹. Column regeneration was reported in the system of Riby et al.[34] but was undertaken manually. (Prior to column regeneration, the water carrier line was disconnected from the rest of the hydride-generation manifold and 1 mol dm⁻³ HCl was pumped through the column to waste.) No indication of sample throughput capabilities were reported.

Another benefit of the proposed manifold design is the potential for automation. By using existing technology, full automation of the system is feasible.[38] Automation of previous systems[33,34] would be difficult without major modifications being made.

By employing the flow injection valve as an interface, the matrix-isolation procedure could be applied to other flow injection hydride-generation manifolds irrespective of their operating variables, gas–liquid separator design or atomization procedures.[18–26]

Conclusion

The use of a flow injection valve as an interface between a continuous flow matrix-removal manifold and a continuous flow hydride-generation manifold allows separate optimization of each procedure so that an interference of up to 1 mg ml⁻¹ of copper in the determination of selenium could be removed. Previous work[16] indicates that with only minor modifications the same system could be used for the determination of other hydride-forming elements in the presence of a variety of interfering species such as Ni, Fe, Co and Ag.

References

1   Smith, A. E., Analyst, 1975, 100, 300.
2   Meyer, A., Hofer, C., Tolg, G., Raptis, S., and Knapp, G., Fresenius Z. Anal. Chem., 1979, 296, 337.
3   Welz, B., and Melcher, M., Analyst, 1984, 109, 569.
4   Welz, B., and Schubert-Jacobs, M., J. Anal. At. Spectrom., 1986, 1, 23.
5   Bax, D., Agterdenbos, J., Worrel, E., and Kolmer, J. B., Spectrochim. Acta. Part B, 1988, 43, 1349.
6   Boampong, C., Brindle, I. D., Le, X.-c., Pidwerbesky, L., and Ceccarelli Ponzoni, C. M., Anal. Chem, 1988, 60, 1185.
7   Kirkbright, G. F., and Taddia, M., Anal. Chim. Acta, 1978, 100, 145.
8   Yamamoto, M., Shohji, T., Kumamaru, T., and Yamamoto, Y., Fresenius Z. Anal. Chem., 1981, 305, 11.
9   Belcher, R., Bogdanski, S. L., Henden, E., and Townshend, A., Analyst, 1975, 100, 522.
10 Peacock, C. J., and Singh, S. C., Analyst, 1981, 106, 931.
11 Bye, R., Engvik, L., and Lund, W., Anal. Chem., 1983, 55, 2457.
12 Bedard, M., and Kerbyson, J. D., Can. J. Spectrosc., 1976, 21, 64.
13 Jones, J. W., Capar, S. G., and O'Haver, T. C., Analyst, 1982, 107, 353.
14 Narasaki, H., and Ikeda, M., Anal. Chem., 1984, 56, 2059.
15 Narasaki, H., Anal. Sci., 1986, 2, 141.
16 Hershey, J. W., and Keliher, P. N., Spectrochim. Acta. Part B, 1989, 44, 329.
17 Pierce, F. D., and Brown, H. R., Anal. Chem., 1977, 49, 1417.
18 Åström, O., Anal. Chem., 1982, 54, 190.
19 Yamamoto, M., Yasuda, M., and Yamamoto, Y., Anal. Chem., 1985, 57, 1382.
20 Chan, C. C. Y., Anal. Chem., 1985, 57, 1482.
21 Ikeda, M., Anal. Chim. Acta, 1985, 167, 289.
22 Pacey, G. E., Straka, M. R., and Gord, J. R., Anal. Chem., 1986, 58, 502.
23 Fang, Z., Xu, S., Wang, X., and Zhang, S., Anal. Chim. Acta, 1986, 179, 325.
24 Yamamoto, M., Takada, K., Kumamaru, T., Yasuda, M., Yokoyama, S., and Yamamoto, Y., Anal. Chem., 1987, 59, 2446.
25 Pettersson, J., Hansson, L., and Olin, Å., Talanta, 1986, 33, 249.
26 McLaughlin, K., Dadgar, D., Smyth, M. R., and McMaster, D., Analyst, 1990, 115, 275.
27 Sweileh, J. A., and Cantwell, F. F., Anal. Chem., 1985, 57, 420.
28 Nord, L., and Karlberg, B., Anal. Chim. Acta, 1981, 125, 199.
29 Olsen, S., Pessenda, L. C. R., Růžička, J., and Hansen, E. H., Analyst, 1983, 108, 905.
30 Kamson, O. F., and Townshend, A., Anal. Chim. Acta, 1983, 155, 253.
31 Martinez-Jimenez, P., Gallego, M., and Valcarcel, M., Analyst, 1987, 112, 1233.
32 Adeeyinwo, C. E., and Tyson, J. F., Anal. Chim. Acta, 1988, 214, 339.
33 Ikeda, M., Anal. Chim. Acta, 1985, 170, 217.
34 Riby, P. G., Haswell, S. J., and Grzeskowiak, R., J. Anal. At. Spectrom., 1989, 4, 181.
35 Welz, B., and Melcher, M., Analyst, 1983, 108, 213.
36 Miller, J. C., and Miller, J. N., in Statistics for Analytical Chemistry, Ellis Horwood, Chichester, 1984, p. 96.
37 Philips Scientific Atomic Absorption Data Book, Philips, Cambridge, 5th edn., 1988, p. 53.
38 Bysouth, S. R., Tyson, J. F., and Stockwell, P. B., J. Autom. Chem., 1989, 11, 36.