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P Becotte-Haigh

JF Tyson

E Denoyer

Flow injection manifold for matrix removal in inductively coupled plasma mass spectrometry by solid phase extraction: determination of Al, Be, Li and Mg in a uranium matrix

Paul Becotte-Haigh,†[a] Julian F. Tyson*[b] and Eric Denoyer[b]

[a]*Department of Chemistry, University of Massachusetts, Box 34510, Amherst, MA 01003–4510, USA*
[b]*Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859, USA*

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A flow injection manifold, incorporating two pumps and an 8-port rotary valve, was developed for the automation of a procedure for the removal of the matrix suppression of uranium on light elements. The procedure was based on the selective retention of the uranium on a column of TRU.Spec® resin (a support material impregnated with a liquid ion-exchanger). The light elements were not retained. The uranium was removed by 0.2 mol l^{-1} ammonium oxalate solution and the column reconditioned by the passage of 25% (v/v) nitric acid. The interference of uranium, 5000 mg l^{-1}, was removed, allowing the determination of aluminium, beryllium, lithium and magnesium at concentrations down to a few μg l^{-1} in 100 μl of sample. The sample acidity was 20% and the carrier stream was 5% with respect to nitric acid. Although higher acid concentrations could have improved the retention of uranium, the acid concentration was not increased to avoid degradation of the nickel sampling and skimmer cones. A complete analysis cycle took 4 min, including the regeneration of the column.

The suppressive effect of heavy matrix elements on the signals from light analyte elements in ICP-MS is a well known interference. Although early investigations[1] considered that ionization suppression might be partially responsible, it was recognized even then that these suppressive effects were more severe than would be expected from ionization suppression alone. It is now considered that the process predominantly responsible for the interference is one of repulsion in the ion beam.[2] This supposition has been supported by model calculations,[3,4] which show that the space charge model predicts the mass dependent trends observed. Methods for overcoming such matrix-induced suppressions have been reviewed[5] and developments may be followed in the recent review literature.[6] Although there are some possibilities for overcoming the effect by either the optimization of the ion lens settings,[7] the use of internal standards[8] (or isotope dilution[9]) or the use of mixed gas plasmas,[10] the most effective approach at present is to separate the analytes from the matrix.

The analyte and matrix may be separated by precipitation, chemical vapor generation, liquid–liquid extraction, liquid–solid extraction and chromatography. Some of these procedures, such as chemical vapor generation, are only applicable to a restricted group of species. All of these procedures may be implemented in the flow injection (FI) mode (or are, in the case of chromatographic separation, already in a FI mode) and there is considerable interest at present[6] in developing FI methodology for such procedures, which otherwise would be time-consuming and tedious, requiring considerable operator intervention. In particular, FI methods based on the use of solid phase reagents packed into low back-pressure microreactors are proving particularly versatile for both separation, preconcentration and even field sampling. In comparison with HPLC, such FI methods are low cost, rapid and easily automated. In addition, many procedures use mainly inorganic reagents and thus problems with the introduction of organic solvents (such as might be needed for a reversed-phase HPLC separation) are avoided. Most of the published FI-solid phase extraction (SPE) procedures have been designed for the retention of the analyte species. In principle, the same chemistry could be used as the basis of a procedure in which the element(s) in question were present in high concentration, thereby constituting a potential interference.

When an FI-SPE procedure is used for the selective retention of the analyte, the relevant issue is selectivity (for the analyte species over the matrix species). Chelating ion-exchange materials, such as immobilized 8-hydroxyquinoline, have been shown to be useful.[11] Often, relatively small amounts (100 mg or less) of material are used but, as the amounts of analyte are also small, the resin capacity is not a limiting factor. However, if the matrix is to be retained, then capacity is also an issue to be considered. It has been shown that, for the relatively small volumes used in typical FI procedures compared with off-line batch procedures, column capacity is not a limiting factor, provided that the manifold is designed so that the column is regenerated during each analysis cycle.[12] In general, the operating characteristics of the manifold are: (a) a controlled sample volume must be delivered on each cycle; (b) residual sample solution must be flushed from the system before the introduction of the next sample; (c) the matrix component must be quantitatively removed from the extractant material; and (d) the extractant must be restored to the initial conditions for the next sample. The goal of the work described in this paper was the development of an automated flow injection (FI) solid phase extraction (SPE) procedure which could be used for the determination of light elements in a uranium matrix.

Several procedures have been used to separate analyte elements from a uranium matrix: precipitation,[13] solid-phase extraction,[14–16] liquid–liquid extraction,[17,18] and HPLC.[19] A solid-phase reagent which has been used to preconcentrate uranium (and other actinides) is TRU.Spec®.[20] The material has also been used in an FI-SPE procedure.[21] The material consists of an inert polymeric substrate, Amberchrom

† Present address: Ion Track Instruments, 340 Fordham Road, Wilmington, MA 01887, USA.

CG-71ms, impregnated with a solution of octyl(phenyl)-*N*,*N*′-diisobutylcarbamoylmethylphosphine oxide in tri-n-butyl phosphate. The material functions as an immobilized liquid ion-exchanger and thus the sorption of most ions increases as the acid concentration increases (unlike the behavior of an immobilized chelating agent). Even at low acidities,[20] the material strongly retains uranium which has to be removed by an appropriate complexing agent. In the FI-SPE procedure, Hollenbach *et al.*[21] determined uranium (and technetium and thorium) in soils by ICP-MS. The uranium was loaded onto a mini-column (containing about 30 mg of TRU.Spec resin) in a carrier stream of 4 mol l^{-1} nitric acid (about 25%) and eluted with 0.1 mol l^{-1} ammonium oxalate. The final acidity of the soil digests for the determination of uranium was also 4 mol l^{-1}.

In this paper, we describe an FI manifold for the automation of the separation of matrix from analyte by retention of the matrix by solid phase extraction in a mini-column. The manifold design allows the direct passage of the analyte species to the spectrometer, the elution of the retained component with one reagent and the regeneration of the column with a second reagent. Volume-based sample introduction was used, allowing the residual previous sample to be flushed from the connecting lines. The manifold use was demonstrated by the determination of light analyte elements in a uranium matrix, which was retained on TRU.Spec resin. The operating conditions were based on the previously published retention and elution behavior of uranium on TRU.Spec,[20,21] but with consideration given to the concentration of nitric acid used.

In a well-designed FI manifold for analyte preconcentration by SPE, the carrier stream and unretained sample components would be diverted to waste during the loading step, thus avoiding any damage to the spectrometer from corrosive reagents or sample matrix components. Following retention of the analyte, the column and connecting lines would be rinsed prior to elution of the retained species and delivery to the spectrometer. Thus, sample acidity could be optimized for species retention. However, when the matrix is to be retained, with direct passage of the analytes to the spectrometer, then the carrier stream and any unretained sample components are also delivered to the spectrometer. The acid concentration used is now constrained by possible instrument damage.

Experimental

Instrumentation

An ELAN 5000 ICP mass spectrometer (Perkin-Elmer SCIEX, Thornhill, ON, Canada) equipped with a FIAS-200 unit (Bodenseewerk Perkin-Elmer, Überlingen, Germany) was used for this work. The FIAS unit was fitted with a two-position rotary valve consisting of 8 ports on the rotor and 8 ports on the stator. The ICP-MS operating conditions are summarized in Table 1. The operating conditions (nebulizer gas flow and ion optics settings) were set while aspirating a solution containing 10 μg l^{-1} of Mg, Rh, Pb and Ce.

The FI manifold is shown in Fig. 1–3. All manifold tubing was 0.51 mm id. The length of tubing between the injection loop and the column was 12 cm. The length of tubing between

Table 1 Operating conditions for the ELAN 5000

Instrumental parameters	
Rf power/W	1125
Argon gas flow:	
Outer gas flow rate/l min^{-1}	15
Intermediate gas flow rate/l min^{-1}	0.80
Aerosol carrier gas flow rate/l min^{-1}	0.9–1.0
Sample and skimmer cones	Nickel
Data acquisition parameters	
Mode	Peak hop transient
Dwell time/ms	40
Points per peak	1
Readings per replicate	150
Number of replicates	4

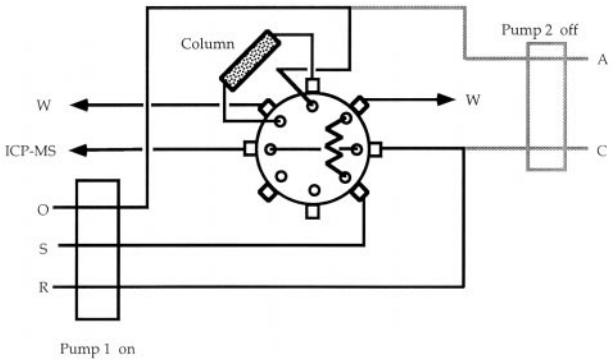

Fig. 1 Flow injection manifold for the removal of a matrix component by solid phase extraction and two-step regeneration of the extractant: step 1. In this step, pump 1 was on and pump 2 was off, and the valve was in position 1 (the 'load' position). Oxalate solution (O) was delivered to the column to remove the accumulated matrix from the previous sample to waste (W). The next sample (S) was flushed through the connecting line, removing the residual previous sample and residual carrier (C) from the sample loop, and rinse solution (R) was delivered to the spectrometer, flushing residual acid from the system.

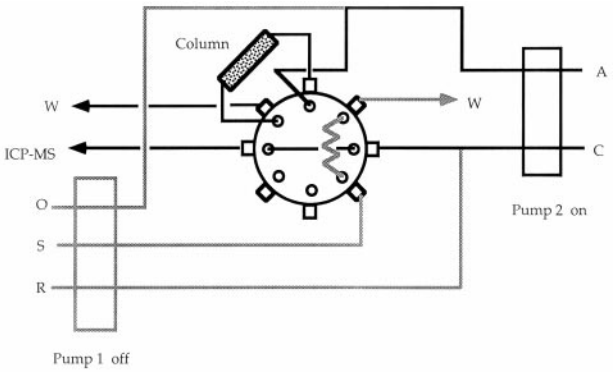

Fig. 2 Flow injection manifold for the removal of a uranium matrix and regeneration of the solid phase extractant, step 2. In this step, pump 1 was off and pump 2 was on and the valve was in the load position. Acid carrier (C) was flushed to the spectrometer and the column was regenerated with 10% nitric acid solution (A).

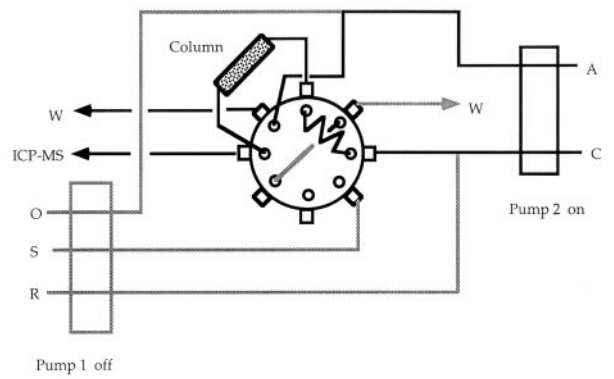

Fig. 3 Flow injection manifold for the removal of a uranium matrix and regeneration of the solid phase extractant, step 3. In this step, pump 1 was off and pump 2 was on and the valve was in position 2 (the 'inject' position). Carrier stream (C) flushed the contents of the sample loop through the column to the spectrometer.

the column and the ICP-MS was 1 m. The injection volume was 100 µl. The outlet of the column was attached to the rotor of the valve so that one end moved when the valve was switched. The time for which the column effluent was directed towards the spectrometer is controlled by the time that the valve was in the 'inject' position. The FIAS operating program is summarized in Table 2. In the pre-sample step, the sample solution was pumped at 0.25 ml min^{-1}, thereby flushing the residue from the previous sample out of the line connecting the autosampler to the valve. In step 1, shown in Fig. 1, the valve was in the 'load' position, pump 2 was off and pump 1 was on, thus filling the sample loop, at 0.5 ml min^{-1}, and delivering ammonium oxalate solution through the column at 6.9 ml min^{-1}, which removed the uranium retained from the previous sample and washed acid from the connecting line (valve to spectrometer) and spray chamber with water. In step 2, shown in Fig. 2, the valve was still in the same position, pump 1 was off and pump 2 was on, regenerating the column with nitric acid (10%, v/v) at 6.9 ml min^{-1} and starting the flow of eluent (5% v/v nitric acid) to the spectrometer at 2.0 ml min^{-1}. In step 3, shown in Fig. 3, the valve was switched to the 'inject' position, pump 1 was still off and pump 2 was still on, the carrier now delivering the contents of the sample loop through the column to the spectrometer.

Reagents

All reagents and samples were prepared with distilled, deionized water (E-Pure, Barnsted, Boston, MA, USA). Fisher Scientific (Fairlawn, NJ, USA) brand ACS Plus grade concentrated nitric acid was used throughout this work. The ammonium oxalate (J.T. Baker, Phillipsburg, NJ, USA) was of 'Baker analyzed' reagent grade.

TRU.Spec resin (Eichrom Industries, Inc., Darien, IL, USA) was loaded into a 4 mm id × 35 mm long plastic chromatography column (Dionex, Sunnyvale, CA, USA). The column held about 150 mg of resin without significant back-pressure. Both ends of the column were plugged with glass wool.

Standards

Magnesium and aluminium certified grade stock standards [1000 mg l^{-1} (m/v) (Fisher, Fairlawn, NJ, USA)] and plasma grade beryllium and lithium stock standards [1000 mg l^{-1} (Johnson Matthey, Ward Hill, MA, USA)] were used. The uranium stock solution used was 10 000 mg l^{-1} in 10% HNO_3 (High Purity Standards, Charleston, SC, USA). A multielement solution of Mg, Al, Be and Li containing 5 mg l^{-1} of each in 4% HNO_3 (v/v) was used to produce calibration standards, which were prepared in 5000 mg l^{-1} uranium and 20% HNO_3. The multielement calibration standard values were 0, 20, 40, 60, 80 and 100 µg l^{-1}. Multielement standards containing 100 µg l^{-1} and 60 µg l^{-1} were prepared in 20% (v/v) nitric acid in both the presence and absence of 5000 mg l^{-1} uranium.

Method development

Optimization. The purpose of the study was to demonstrate the feasibility of the manifold design and so only a limited amount of optimization was carried out. Suitable starting values of relevant parameters were available from previous work on the retention and elution behavior of uranium and TRU.Spec.[20,21] The figures of merit were adequate retention of uranium, and precision while keeping the nitric acid concentration delivered to the spectrometer to a minimum. Parameters that were studied were: the concentration of nitric acid in the carrier stream (0–5%), the concentration of nitric acid in the column regeneration solution (5–20%), the concentration of ammonium oxalate used to strip the uranium from the column (0.1–0.2 mol l^{-1}), and the time of the stripping step (1–3 min). These latter two parameters were considered interactive, and were studied by a factorial method.[22] Other parameters were considered independent, and a univariate search procedure was used for the study of these. The nitric acid concentration in the carrier stream was limited to 5% to avoid degradation of the nickel sampler and skimmer cones.

The signals from a 60 µg l^{-1} multi-element standard in 5000 mg l^{-1} of uranium, injected into a single-line manifold and directly transported to the spectrometer, were investigated for sample volumes of 60 and 100 µl, and a carrier flow rate of 2 ml min^{-1}.

Horwitz *et al.*[20] reported that the experimentally measured capacity of the material was 4.1 mg of Nd or 6.8 mg of Am per ml of bed, and that the bed density was 0.370 g ml^{-1}. The volume of the bed used here was about 440 µl, so that for a resin mass of 150 mg, the bed density was 0.34 g ml^{-1}, in reasonable agreement with the literature value. Thus, the capacity of the resin in the column was conservatively estimated to be about 2 mg of uranium. For a sample solution containing 5000 mg l^{-1} of uranium, a 100 µl injection volume introduces 0.5 mg of uranium. The injection volume was thus fixed at 100 µl. The sample acidity was kept at 20%, slightly lower that the 25% (4 mol l^{-1}) used in the previously reported study of the preconcentration of uranium on TRU.Spec.[20]

Table 2 FIAS 200 program

Step	Time/s	Pump 1/ rev min^{-1}	Pump 2/ rev min^{-1}	Valve position
Pre-sample	10	40	0	1
1	120	80	0	1
2	60	0	80	1
3	40	0	80	2

Results and discussion

The best precision was obtained with 5% nitric acid in the carrier, passing 0.2 mol l^{-1} ammonium oxalate for 2 min to remove the uranium and 10% nitric acid for 1 min to regenerate the column. The two-minute stripping time was sufficient for the connecting lines to be flushed and the injection loop to be filled with the next sample (see Fig. 1).

The averages of four traces for a 60 µg l^{-1} multielement standard in 5000 mg l^{-1} uranium and 20% nitric acid are shown in Fig. 4. The uranium-238 signal at the analyte peak maxima (approximately 24 s) was about 2000 cps, which allowed determinations based on peak height to be made.

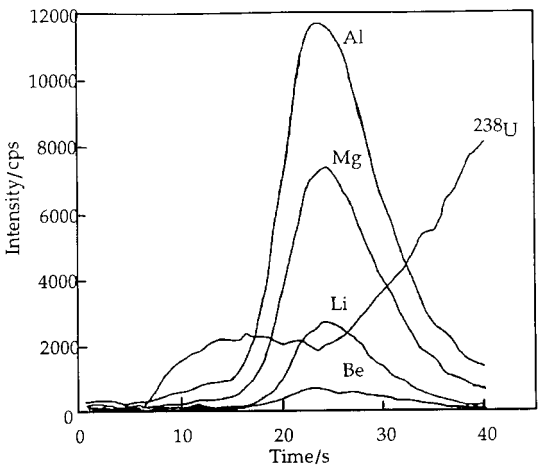

Fig. 4 Average of four traces for injections of a 60 µg l^{-1} multielement standard containing 5000 mg l^{-1} uranium and 20% nitric acid.

As the dispersion coefficient, D, of the manifold was approximately 5, at the peak maximum the injected analyte and interferent concentrations have been reduced by a factor of 5 to approximately 12 $\mu g\,l^{-1}$ and 1000 $mg\,l^{-1}$, respectively. The acid concentration can be estimated from the combined contribution of the acid in the carrier (reduced by a factor of $D/(D-1)$, the reagent dispersion coefficient[23]) and that in the sample (reduced by a factor D) to be 8%. However, due to the differences in diffusion coefficients between those for the metal ions and that for the hydronium ion, the peak maximum for the acid will not coincide with that for the analytes. During the regeneration stage, the column was flushed with 10% acid whereas, in an effort to minimize the amount of acid delivered to the instrument, the nebulizer and spray chamber were flushed with water during the filling of the sample injection loop (see Fig. 1) followed by 5% nitric acid carrier during the regeneration stage (see Fig. 2). The rise in uranium signal at about 6 s (see Fig. 4.) may have been due to the mobilization of uranium from the interior of the spray chamber when the valve was switched to the inject position, whereupon the residual 10% acid is flushed out of the column by the carrier (followed by the acid from the sample and the acid in the carrier). As the tubing between the valve and the nebulizer is 1 m long $\times$ 0.51 mm id (volume 0.2 ml) it may be calculated that, at a flow rate of 2 $ml\,min^{-1}$, the average time for the leading edge of this acid zone to traverse the connecting tubing is 6 s. According to Horwitz *et al.*,[20] the void volume of the bed is 0.68 ml per ml of bed and thus the volume of 10% acid in the column is about 300 µl. For this 'injection' volume, the dispersion coefficient would be about 1.5–2. Thus, when the valve was switched to the inject position, a rather complex acid concentration profile would have been presented to the instrument, consisting of the dispersed boundaries between 5% nitric acid (in the carrier), 300 µl of 10% acid (in the column), 100 µl of 20% acid (from the sample) and 5% acid (in the carrier), in that order.

When the 60 $\mu g\,l^{-1}$ standard in 5000 $mg\,l^{-1}$ uranium was introduced into the spectrometer *via* the single-line manifold, the analyte signals, for both the 60 and the 100 µl injection volumes, were almost completely suppressed. The dispersion coefficients were estimated to be 5.4 and 3.4, respectively, giving uranium concentrations at the peak maxima of 930 $mg\,l^{-1}$ and 1500 $mg\,l^{-1}$, respectively. This suppressive effect of the uranium is in line with that observed by Pilon *et al.*, who reported[24] a suppression of about 80% in the signal for 100 $\mu g\,l^{-1}$ Be in the presence of 900 $mg\,l^{-1}$ uranium.

As can be seen from Fig. 4, the uranium apparently began to elute shortly after the unretained analyte ions. To avoid the introduction of large amounts of uranium to the spectrometer, the valve was switched after 40 s and the elution process accelerated by the passage of the ammonium oxalate solution. The relatively rapid elution of the uranium is contrary to what would have been expected, based on the results obtained by Horwitz *et al.*,[20] who reported that, for a 5% nitric acid eluent, it required approximately 1000 column void volumes to reach the peak maximum of the eluting uranium (at a flow rate of approximately 1–2 $ml\,min^{-1}$). This capacity factor corresponds to 30 ml for the column used here. Although the uranium peak is undoubtedly very broad (with a basewidth of possibly as large as 80 column volumes), it is considered unlikely that the leading edge of the peak would be observed after only the passage of 3 column volumes. It is possible that some uranium is eluted due to the transition from the 20% acid sample zone to the 5% acid carrier, or that the capacity of the column is not as great as expected and the rise in signal for uranium indicates breakthrough. It is also possible that the column may have developed channels, allowing some uranium to pass directly through the column. As the stationary phase is not covalently bonded to the support material, it is expected that the capacity of the column would decrease over time as the stationary phase is washed out of the most accessible resin pores.

Visual inspection of the calibration plots for the four analytes indicated that they were linear over the range 1–100 $\mu g\,l^{-1}$ (with correlation coefficients between 0.993 and 0.999). Detection limits in the presence of 5000 $mg\,l^{-1}$ uranium, based on the concentrations corresponding to the standard deviations of signals from 7 replicate injections of a blank solution, were 0.6, 5, 1 and 3 $\mu g\,l^{-1}$ for Al, Be, Li and Mg, respectively. There was some evidence that the uranium solution was contaminated with the analytes, as significantly higher signals (based on a t-test at 95% confidence) would be obtained for some standards in the presence of the uranium compared with the signals obtained for the same concentration in the absence of uranium. For Li and Be, the calibrations in the presence of uranium (a standard additions analysis of the uranium solution) had positive intercepts that were significantly different from zero, indicating the presence of a few $\mu g\,l^{-1}$ of these elements in the uranium standard.

Conclusions

The manifold design allows the automation of a solid phase extraction procedure for separation of analyte and matrix species by retention of the analyte, followed by a two-step regeneration of the extractant. The TRU.Spec resin chemistry that has been used for the preconcentration of uranium[21] may be adapted to the removal of uranium when present in concentrations up to 5000 $mg\,l^{-1}$. The tolerance to uranium on this basis, which is a function of both sample injection volume and resin capacity, is higher than that reported for the HPLC procedure by Jiang *et al.*,[15] who were limited to 470 $mg\,l^{-1}$ by the solubility of the uranium complex used. However, the TRU.Spec resin may have a limited lifetime due to loss of the adsorbed stationary phase, and a more robust procedure would be based on a covalently bonded functionality. Better performance might have been obtained if the column had been replaced more frequently and the spray chamber had been continually washed with nitric acid solution. The discrepancy between the retention/elution behaviour of uranium found in this study and that reported previously[20] merits further investigation.

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References

1 J. A. Olivares and R. S. Houk, *Anal. Chem.*, 1986, **58**, 20.
2 G. R. Gillson, D. J. Douglas, J. E. Fulford, K. W. Hallikan and S. D. Tanner, *Anal. Chem.*, 1988, **60**, 1472.
3 S. D. Tanner, *Spectrochim. Acta, Part B*, 1992, **47**, 809.
4 S. D. Tanner, in *Plasma Source Mass Spectrometry: Developments and Applications*, ed. G. Holland and S. D. Tanner, Royal Society of Chemistry, Cambridge, 1997, pp. 13–17.
5 E. H. Evans and J. J. Giglio, *J. Anal. At. Spectrom.*, 1993, **8**, 1.
6 J. R. Bacon, J. S. Crain, A. W. McMahon and J. G. Williams, *J. Anal. At. Spectrom.*, 1997, **12**, 407R.
7 E. H. Evans and J. A. Caruso, *Spectrochim. Acta, Part B*, 1992, **47**, 1001.
8 J. J. Thompson and R. S. Houk, *Appl. Spectrosc.*, 1987, **41**, 801.
9 J. D. Fasset and P. J. Paulsen, *Anal. Chem.*, 1989, **61**, 643A.
10 D. Beauchemin and J. M. Craig, *Spectrochim. Acta, Part B*, 1991, **46**, 603.
11 J. W. McLaren, A. P. Myktykiuk, S. N. Willie and S. S. Berman, *Anal. Chem.*, 1985, **57**, 2907.
12 J. F. Tyson, S. G. Offley, N. J. Seare, H. A. B. Kibble and C. Fellows, *J. Anal. At. Spectrom.*, 1992, **7**, 315.
13 G. E. M. Hall, J. C. Pelchat and J. Loop, *J. Anal. At. Spectrom.*, 1990, **5**, 339.

14 F. Nakashima, *Anal. Chim. Acta*, 1964, **30**, 167.
15 C. E. Pietri and A. W. Wenzel, *Anal. Chem.*, 1963, **35**, 209.
16 E. A. Huff, *Anal. Chem.*, 1965, **37**, 533.
17 M. D. Palmieri, J. S. Fritz, J. J. Thompson and R. S. Houk, *Anal. Chim. Acta*, 1986, **184**, 187.
18 F. Nakashima, *Anal. Chim. Acta*, 1964, **30**, 255.
19 S. J. Jiang, M. D. Palmieri and R. S. Houk, *Anal. Chim. Acta*, 1987, **200**, 559.
20 E. P. Horwitz, R. Chiarizia, M. L. Dietz, H. Diamond and D. M. Nelson, *Anal. Chim. Acta*, 1993, **281**, 361.
21 M. Hollenbach, J. Grohs, S. Mamich, M. Kraft and E. R. Denoyer, *J. Anal. At. Spectrom.*, 1994, **9**, 927.
22 J. C. Miller and J. N. Miller, *Statistics for Analytical Chemistry*, Horwood, Chichester, 2nd edn., 1988, p. 175.
23 J. F. Tyson, *Anal. Chim. Acta,* 1986, **179**, 131.
24 F. Pilon, D. Koller and A. Raith, in *Plasma Source Mass Spectrometry: Developments and Applications*, ed. G. Holland and S. D. Tanner, Royal Society of Chemistry, Cambridge, 1997, pp 44–50.

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