Comparison of Sodium Chloride and Magnesium Chloride Interferences in Continuum Source Atomic Absorption Spectrometry With Wall, Platform and Probe Electrothermal Atomization

John Carroll,* **Nancy J. Miller-Ihli and James M. Harnly**
US Department of Agriculture, Nutrient Composition Laboratory, BARC-East, Beltsville, MD 20705, USA

Thomas C. O'Haver
Department of Chemistry, University of Maryland, College Park, MD 20742, USA

David Littlejohn†
Department of Pure and Applied Chemistry, University of Strathclyde, Cathedral Street, Glasgow G1 1XL, UK

Various masses between 10 and 500 μg of NaCl or $MgCl_2$ were added to 1 ng of Cr, Cu and Mn, 2 ng of Cd and Pb and 4 ng of Co, Mo, Ni and V to study the interferences encountered when wall, platform and probe atomization are applied in continuum source electrothermal atomic absorption spectrometry. No char step was used and a compromise atomization temperature of 2700 °C was selected for simultaneous multi-element measurements. No great difference was observed in the analyte signal recovery values obtained with the three atomization modes when NaCl was the interferent. However, with $MgCl_2$, greater interferences were observed with wall atomization. Overall, probe atomization proved as good as, if not better than platform atomization for the elements considered. With both procedures, freedom from NaCl or $MgCl_2$ interferences was achieved at chloride salt:analyte mole ratios of 1×10^3–1×10^5. Although it was not possible to make a definitive assessment of the procedures responsible for the interferences observed, there was some evidence that vapour-phase chemical effects are more important for $MgCl_2$ than for NaCl, occlusion of Cd, Mn and Pb occurs in NaCl and expulsion of Co, Cr, Cu, Mn and Ni occurs due to co-vaporization with NaCl.

Keywords: *Continuum source atomic absorption spectrometry; electrothermal atomization; simultaneous multi-element measurement; sodium chloride and magnesium chloride interference effect*

The emergence of continuum source atomic absorption spectrometry (CSAAS) has, for the first time, enabled the analytical sensitivity afforded by an electrothermal atomizer to be exploited on a truly simultaneous multi-element basis.[1-3] The simultaneous multi-element AAS with continuum source (SIMAAC) instrument developed by Harnly et al.,[4] employed a 300 W xenon-arc continuum lamp as the source, with a high resolution échelle polychromator for spectral detection. Computer controlled wavelength modulation allowed the acquisition and calculation of background corrected absorbances on up to 16 channels. The detection limits obtained were comparable to those of conventional line source AAS for elements with resonance lines above 280 nm. Below this wavelength, however, detection limits were poorer owing to the reduction in intensity of the continuum source and the lower spectral efficiency of the échelle spectrometer in this wavelength region.

With electrothermal SIMAAC a restriction is normally placed on the choice of char and atomization temperatures that can be applied, especially when elements of widely differing volatility are determined. In particular, if comparatively volatile elements are present in the sample, the maximum char temperature may be restricted to a value that, for many matrices, does not allow the bulk of the sample to be removed prior to the atomization step. The use of chemical modifiers[5,6] can improve the situation, but care must be taken to avoid the occurrence of spectral overlap interferences by high concentrations of magnesium,[7] added in the form of $Mg(NO_3)_2$, and the introduction of high blank contamination levels of some elements.

Thus, under the conditions required for simultaneous multi-element analysis, the residual matrix levels present during the atomization step may be significantly higher than would normally be observed under optimized conditions for single element determinations. Consequently, any electrothermal atomization procedure employed for this purpose should be capable of limiting matrix interference effects in addition to providing satisfactory sensitivity for all the elements to be determined.

Recent developments in electrothermal atomization technology have centred on procedures which establish high temperature conditions in the atomizer prior to the release of the analyte into the vapour phase. This leads to improved dissociation of any molecules containing the analyte and reduces interferences caused by interaction with matrix salts (*e.g.*, chlorides). Procedures such as platform,[8,9] probe[10,11] and two-step[12,13] atomization have been shown to be effective in reducing matrix interferences. Harnly and Kane[1] have shown that for wall and platform atomization in CSAAS, the atomization temperature must have a high bias in favour of efficient atomization of the more refractory elements. Under such conditions, release of volatile and medium volatile elements may occur before the atomizer temperature has stabilized and this can reduce the effectiveness of the platform procedure in minimizing chemical interferences. The problem can be avoided if the sample is introduced into the atomizer after constant temperature conditions have been established. This can be achieved with the two-step constant temperature atomizer[12,13] and probe atomization.[10,11] Lundberg et al.[14] reported that it was difficult to select compromise atomization conditions for a two-step atomizer, which gave maximum sensitivity in CSAAS for elements of different volatility. However, lower background absorption levels, carry-over contamination and halide interferences were obtained compared with conventional atomization procedures. At present the two-step atomizer seems to be the

---

*On study leave from the University of Strathclyde. Present address, ICI Wilton Materials Research Centre, P.O. Box 90, Wilton, Middlesborough, Cleveland TS6 8JE, UK.
†To whom correspondence should be addressed.

most attractive system for multi-element analysis by electrothermal CSAAS (ET-CSAAS), although the need for a special atomizer and two power supplies might limit its general use.

Previous studies using probe atomization[15] for simultaneous multi-element analysis by CSAAS have shown that at the compromise atomization temperature selected (2700 °C), similar detection limits (within a factor of four) were achieved for 12 elements with wall and probe atomization. However, the probe gave better detection limits than the platform for eight of the elements studied, and the performance was similar for the four other analytes. It was suggested that in comparison with the other procedures used with a conventional atomizer design, probe atomization might offer some advantages in CSAAS over tube, wall and platform atomization, as it gives satisfactory sensitivity and might offer better control of chemical interferences. No evidence was given to substantiate the latter point, so in the present study the performance of wall, platform and probe atomization has been compared with respect to the extent of chemical interferences on nine elements caused by NaCl and MgCl$_2$, added at concentrations of up to 5% m/v. The same compromise conditions were applied for each mode of atomization and the nine elements were measured simultaneously using the SIMAAC system. No char step was used in the furnace programme, so the mass of interferent present during atomization was the same for all elements and with each procedure.

Several different processes can cause a decrease in the magnitude of the signal when the analyte elements are vaporized in the presence of NaCl or MgCl$_2$. (*i*) A true gas-phase interference can occur whereby analyte atoms and chlorine-containing species from the matrix salts react to form gaseous metal chlorides, thereby reducing the free metal concentration in the atomizer volume. (*ii*) A condensed-phase interference can occur, resulting in the volatilization of the analyte as a chloride molecule, which is removed from the absorption volume without being atomized to the same extent as for an interferent-free solution. (*iii*) A combination of (*i*) and (*ii*) can occur. The analyte and matrix are volatilized as chloride molecules and dissociation of the analyte chloride is suppressed owing to the mass action effect of the excess of chlorine-containing species produced by the interferent matrix. At any temperature and chloride salt concentration, the extent of the interference for different elements is likely to depend on the dissociation energy of the monochloride. Elements with a low dissociation energy will probably suffer the least interference. (*iv*) The matrix salts may cause occlusion of the analyte, which can reduce the atomization efficiency and cause loss of the analyte by a carrier mechanism. (*v*)

Rapid evolution of vapours from the comparatively large mass of matrix salts may cause expulsion of the analyte species from the absorption volume and so give a reduction in the atomic absorption signal of the analyte.

This study compares the interferences caused by NaCl and MgCl$_2$ when wall, platform and probe atomization are used for ET-CSAAS. The results obtained suggest that more than one of the above processes occur and that there are some differences in the mechanisms of the NaCl and MgCl$_2$ interferences.

Experimental

Spectrometer

The SIMAAC system used for simultaneous multi-element measurements has been described previously.[1-4] The instrument consists of a 300 W xenon lamp as the primary source, an échelle polychromator modified for wavelength modulation and a PDP 11/34 mini-computer. The mini-computer generated the modulation waveform and performed data acquisition for up to 16 elements. In the present study, absorbance measurements were made simultaneously for Cd (228.8 nm), Co (240.7 nm), Cr (357.9 nm), Cu (324.8 nm), Mn (279.5 nm), Mo (313.3 nm), Ni (232.0 nm), Pb (283.3 nm) and V (318.4 nm).

Electrothermal Atomizer

A Perkin-Elmer HGA-500 electrothermal atomizer was used with an automatic graphite probe assembly, which has been documented previously.[15] For probe atomization studies, pyrolytic graphite coated microporous glassy carbon probes were employed for all measurements. Details of the analytical performance of this probe material have been published.[16] Platforms were fabricated from pyrolytic graphite tubes using the method outlined by Koirtyohann and Kaiser.[17] Although the platforms were slightly different in dimensions and design from commercial equivalents, the platforms were used as per current convention, in that the edges were in minimal contact with the tube surface. Pyrolytic graphite coated electrographite tubes were used for all wall, platform and probe measurements. With probe atomization, a small slot was made in the graphite tube wall beneath the injection hole to allow entry and exit of the probe head. Sample aliquots (10 mm^3) were deposited onto the atomization surface (wall, platform or probe) using a Perkin-Elmer AS-I autosampler.

Table 1 Atomizer temperature programmes

Step	Temperature/ °C	Ramp time/ s	Hold time/ s	Conditions
Dry				
Wall	120	5	45	—
Platform	250	—	—	—
Probe	450	—	—	—
Pre-atomize				
Probe	2700	0	5	RC*
Atomize	2700	0	5	R†, GS‡
Clean	2700	0	5	

*RC = recorder function selected, in this instance to initiate removal of the probe.
†R = spectrometer read.
‡GS = argon internal gas flow stopped; 300 cm^3 min^{-1} at all other steps.

Table 2 Comparison of NaCl interferences for wall, platform and probe atomization using SIMAAC

| | | | Interferent level/μg | | | | |
| | | | 10 | 50 | 100 | 200 | 500 |
Element	Analyte mass/ng	Atomization			Signal recovery* (%)		
Cd	2	Wall	100	80	70	55	ND†
		Platform	90	65	65	60	64
		Probe	100	65	65	60	60
Co	4	Wall	95	75	40	20	ND
		Platform	95	70	50	30	25
		Probe	100	55	45	30	25
Cr	1	Wall	85	65	35	25	ND
		Platform	95	65	50	40	25
		Probe	100	65	50	40	25
Cu	1	Wall	85	50	40	35	ND
		Platform	95	65	55	55	50
		Probe	100	85	75	70	55
Mn	1	Wall	65	30	15	15	ND
		Platform	100	60	40	30	10
		Probe	100	65	50	40	40
Mo	4	Wall	50	70	80	85	ND
		Platform	50	40	45	45	45
		Probe	105	105	95	75	50
Ni	4	Wall	105	85	65	50	ND
		Platform	90	65	60	45	30
		Probe	100	65	60	40	30
Pb	2	Wall‡	82	85	92	86	ND
		Platform‡	90	65	40	58	48
		Probe	100	100	100	100	65
V	4	Wall	95	95	70	30	ND
		Platform	95	70	55	30	25
		Probe	105	65	40	25	5

*Based on integrated absorbance signals.
†ND = not determined.
‡Recoveries of 95 and 100% for wall and platform atomization, respectively, with 5 μg of NaCl.

Electrothermal Atomizer Operating Conditions

The operating parameters for each mode of atomization are given in Table 1. Since the nature of simultaneous multi-element measurements precludes the use of a high char temperature when volatile elements are present, it was decided to omit the char stage for the purposes of the present study, rather than remove the volatile elements from the list of test analytes. Similarly, a compromise atomization temperature of 2700 °C was employed for all modes of atomization as this had previously been shown to provide satisfactory analytical performance when elements were determined on a simultaneous basis.[1,15]

Calibration Solutions

Multi-element test solutions were prepared from multi-element stock solutions (Spex Industries). Stock solutions containing 10% m/v NaCl and 10% m/v $MgCl_2$ were prepared for the interference studies by dissolving the appropriate amount of pure salt in ultra-pure distilled water. For the $MgCl_2$ solution, spectroscopic-grade MgO was reacted with an appropriate volume of Ultrex HCl. This procedure was necessary owing to the unacceptably high analyte blank levels present in the AnalaR grade $MgCl_2$ salt. When analyte blank levels were measured in the prepared interferent salt solutions, it was discovered that it would not be possible to conduct interference studies for all 16 elements investigated previously[1,15] because of the high blank levels for some elements. For this reason the number of test analytes in the present study was restricted to nine. Appropriate solutions of these elements were prepared by serial dilution from multi-element stock solutions to give final elemental concentrations of 100 μg dm^{-3} for Cr, Cu and Mn, 200 μg dm^{-3} for Cd and Pb, and 400 μg dm^{-3} for Co, Mo, Ni and V. The different analyte concentrations were required because of differences in the SIMAAC sensitivity for the elements. The NaCl and $MgCl_2$ solutions used in the interference study were 0.1, 0.5, 1.0, 2.0 and 5.0%.

Results and Discussion

The effects of NaCl or $MgCl_2$ on the integrated absorbance values of the nine test elements were measured simultaneously using the SIMAAC system. Recoveries of the analyte signals obtained in the presence of the interferent salts were calculated relative to the integrated absorbance signals produced by the same mass of analyte injected in an interferent-free solution (all signals were corrected for the blank). The peak height absorbance values were in the range 0.05–0.3. Recoveries were calculated from the mean result of three replicate measuremens and it was assumed that values in the range 90–110% indicated freedom from interference.

Tables 2 and 3 summarize the results obtained with NaCl and $MgCl_2$, respectively, as the interferent. With NaCl, there was no great difference in the signal recovery values for Cd, Co, Ni and V when wall, platform or probe atomization was used, and the wall atomization results were only slightly poorer than those of the other two procedures for Cr, Cu and Pb. The recovery values for Mn and Mo were best with probe atomization, although similar performance was obtained for Mn with the platform.

Different trends were noted when $MgCl_2$ was used as the interferent (Table 3). Only the more refractory elements Cr,

Table 3 Comparison of MgCl₂ interferences for wall, platform and probe atomization using SIMAAC

| | | | Interferent level/μg | | | | | |
| | Analyte | | 5 | 10 | 50 | 100 | 200 | 500 |
Element	mass/ng	Atomization			Signal recovery* (%)			
Cd	2	Wall	55	55	45	40	35	20
		Platform	75	45	60	50	40	45
		Probe	100	90	80	50	45	30
Co	4	Wall	45	30	15	5	5	0
		Platform	110	105	105	85	65	60
		Probe	105	110	100	75	70	60
Cr	1	Wall	95	95	95	80	75	75
		Platform	100	100	70	55	35	35
		Probe	100	95	65	45	40	25
Cu	1	Wall	40	25	20	20	25	15
		Platform	100	100	85	65	50	40
		Probe	105	100	80	70	70	60
Mn	1	Wall	35	20	10	10	3	5
		Platform	95	80	40	30	20	15
		Probe	95	90	80	50	45	35
Mo	4	Wall	90	90	85	70	75	75
		Platform	75	80	95	70	65	55
		Probe	115	110	105	90	95	75
Ni	4	Wall	70	55	30	25	25	25
		Platform	110	110	100	75	55	50
		Probe	110	110	95	75	75	50
Pb	2	Wall	5	0	0	0	0	0
		Platform	ND†	100	ND	75	50	35
		Probe	100	100	85	75	75	60
V	4	Wall	100	95	80	75	70	75
		Platform	105	105	80	55	50	40
		Probe	110	110	85	50	55	25

*Based on integrated absorbance signals.
†ND = Not determined.

Table 4 Maximum chloride salt:analyte mole ratios without interference, using SIMAAC with platform and probe atomization

| | | Maximum interferent:analyte mole ratio without interference† | | | | |
| | Atom appearance | NaCl | | MgCl₂ | | M–Cl dissociation energy‡/ |
Element	temperature*/°C	Platform	Probe	Platform	Probe	kJ mol⁻¹
Cd	460	9.6×10^3	9.6×10^3	$<1 \times 10^3$	5.9×10^3	208
Pb	790	1.8×10^4	3.5×10^5	1.1×10^4	1.1×10^4	301 ± 29
Cu	1080	1.1×10^4	1.1×10^4	6.6×10^3	6.6×10^3	383 ± 5
Mn	1240	9.4×10^3	9.4×10^3	5.9×10^3	5.9×10^3	361 ± 10
Co	1370	2.5×10^3	2.5×10^3	7.7×10^3	7.7×10^3	389
Ni	1400	2.5×10^3	2.5×10^3	7.7×10^3	7.7×10^3	372 ± 21
Cr	1470	8.9×10^3	8.9×10^3	5.5×10^3	5.5×10^3	366 ± 24
V	2000	2.2×10^3	2.2×10^3	1.4×10^3	1.4×10^3	477 ± 63
Mo	1970	$<4 \times 10^3$	4.1×10^4	1.3×10^4	5.0×10^4	NA§

*Ref. 18.
†Based on results in Tables 2 and 3.
‡Refs. 18 and 19; errors not available for Cd–Cl and Co–Cl values.
§NA = Not available.

Mo and V exhibited similar signal recovery values for each mode of atomization. The interferences observed for Cd, Co, Cu, Mn, Ni and Pb were greater, in general, with wall atomization than for the platform or probe methods. For most of the analytes the signal recovery values obtained with the platform and probe were similar, although the probe method was superior for Cd and Mn.

The differences in the NaCl and MgCl₂ results indicate that the interference mechanisms of the two salts might be different. With platform and probe atomization, the tem-perature of the gas at the time of analyte vaporization is usually higher than for wall atomization. This appears to be an important factor in determining the extent of MgCl₂ interferences on the more volatile elements, but is appar-ently less important with NaCl. This suggests that vapour-phase interference effects, such as those implicit in mecha-nisms (i) and (iii) mentioned earlier, may be more impor-tant for MgCl₂.

The extent of vapour-phase chemical interferences de-pends on the dissociation energies of the analyte mono-

chlorides as well as the gas temperature. If vapour-phase effects are important, some correlation should exist between the order of interferences caused by NaCl and $MgCl_2$ and the dissociation energies of the analyte monochlorides. The platform and probe results given in Tables 2 and 3 were used to obtain the mole ratios of chloride to analyte at which interferences were first observed. The data are presented in Table 4, along with the analyte atom appearance temperatures[18] and the monochloride dissociation energies.[18,19] The trends exhibited by the probe and platform results are similar. With NaCl, the order of interference for probe atomization is $(V=Ni=Co)>(Cr=Mn=Cd=Cu)>Mo>Pb$. With $MgCl_2$, the corresponding order is $V>(Cr=Cd=Mn=Cu=Co=Ni)>Pb>Mo$. The dissociation energy values given in Table 4 suggest that the expected order of interference should be $V>(Co=Cu=Ni=Cr=Mn)>Pb>Cd$. Neither of the observed trends correlate well with the order suggested from a consideration of the monochloride dissociation energies, but the agreement is better for $MgCl_2$ than for NaCl. Cadmium is possibly less affected by the chloride salts owing to its volatility, which may cause the element to be vaporized in advance of the interferent, such that the temporal overlap of the analyte and chloride vapours in the atomizer tube is less than for the other elements.

Expulsion of the analyte vapours with the matrix gases is also a possible cause of chloride salt interferences. Holcombe[20] has argued that vapour expulsion becomes significant as an interference mechanism only if there is near coincidence in the volatilization temperature of the analyte and matrix species and when more than 1×10^{-6} moles of matrix gas are evolved. It is known that NaCl can be vaporized from a platform above 800 °C[21] and that the volatilization of the salt is almost complete by 1000 °C. Sodium atoms are produced at about 980 °C and Welz et al.[22] have suggested that the flow of Na atoms generated by 100 μg of NaCl can cause rapid expulsion of Pb from an electrothermal atomizer tube. It is possible, therefore, that elements with appearance temperatures similar to or slightly greater than that of Na may also be removed by the excess of flow of the Na atoms (or NaCl molecules), which is likely to persist for 1 or 2 s at high NaCl masses. Of the elements included in this study, Co, Cr, Cu, Mn and Ni have appearance temperatures slightly greater than Na and so the on-set of interference should occur at the same NaCl mass for these elements. The results in Table 2 indicate that this occurs for platform and probe atomization and, with the exception of Mn, also for wall atomization.

Shifts in the time of the peak AAS signal were observed for some elements with probe atomization in the presence of NaCl, suggesting that suppression of analyte vaporization might also occur by occlusion of the analyte in the NaCl matrix. For Cd, the peak time increased from 100 (no NaCl) to 140 ms with 10 μg of NaCl and to 360 ms with 100 μg of NaCl. For Pb, the peak time changed from 140 to 180 to 250 ms and for Mn, the change was from 180 to 210 to 290 ms, as the NaCl mass was increased from 0 to 10 μg and then to 100 μg. Cadmium, Mn and Pb are the most volatile of the elements studied and so are more likely to be affected by occlusion in the NaCl matrix. This effect was not observed with $MgCl_2$ as the interferent. The result for Pb is different to that observed by Welz et al.[22] who reported that the Pb peak occurred earlier in the presence of NaCl when vaporized from a platform. It is possible that the peak shifts could also arise owing to complete temporal overlap in the vaporization of the analyte and NaCl, which for a short period, caused total suppression of atom formation. However, $MgCl_2$ would also be expected to exhibit this effect and cause peak shifts.

Conclusions

The NaCl interference study indicated that the platform and probe atomization procedures had only a slight advantage over wall atomization for the majority of the elements considered. With $MgCl_2$, however, the interference effects observed with wall atomization were generally more severe than for the other two procedures, which were similar in performance. Overall, the analyte signal recovery values obtained with probe atomization were similar to, if not better than, those obtained with platform atomization.

As a char step was not included in the atomizer programme, the interference processes which caused a reduction in the analyte signals must have occurred during the atomization stage. It is probable that a number of phenomena contributed to the interference observed. A comparison of the $MgCl_2$ results for the three modes of atomization suggests that, under the conditions used for the SIMAAC measurements, vapour-phase chemical interferences could be important with this salt. There was some evidence that occlusion of Cd, Mn and Pb in NaCl might have contributed to the interferences experienced by these elements. Also, expulsion of Co, Cr, Cu, Mn and Ni by rapid production of NaCl or Na vapours may have reduced the maximum analyte atom concentration achieved in the furnace. It is concluded therefore, that gas expulsion, analyte occlusion and vapour-phase effects all contribute to the interferences observed. However, it is not possible from this study to determine the relative contribution of each process to the interferences suffered by the various analyte elements.

Without a char step, freedom from interference was achieved with probe or platform atomization for interferent:analyte mole ratios of up to $1 \times 10^3 - 1 \times 10^5$. Greater freedom from interference may be obtained with chemical modification. A recent study with Pd as the modifier has indicated that a compromise char temperature of 800 °C can be used for simultaneous determination of Cd, Cr, Cu, Mn, Mo and Pb by ET-CSAAS with wall atomization,[23] although contamination of the sample by the modifier can be a problem.

References

1 Harnly, J. M., and Kane, J. S., Anal. Chem., 1984, **56**, 48.
2 Harnly, J. M., Miller-Ihli, N. J., and O'Haver, T. C., Spectrochim. Acta, Part B, 1984, **39**, 305.
3 O'Haver, T. C., Analyst, 1984, **109**, 211.
4 Harnly, J. M., Miller-Ihli, N. J., and O'Haver, T. C., Appl. Spectrosc., 1982, **36**, 637.
5 Ediger, R. D., At. Absorpt. Newsl., 1974, **14**, 127.
6 Slavin, W., Manning, D. C., and Carnrick, G. R., At. Spectrosc., 1981, **2**, 137.
7 MacDonald, L. R., O'Haver, T. C., Ottaway, B. J., and Ottaway, J. M., J. Anal. At. Spectrom., 1986, **1**, 485.
8 Slavin, W., Carnrick, G. R., Manning, D. C., and Pruzkowska, E., At. Spectrosc., 1983, **4**, 69.
9 Slavin, W., and Manning, D. C., Spectrochim. Acta, Part B, 1980, **35**, 701.
10 Ajayi, O. O., Littlejohn, D., and Boss, C. B., Anal. Proc., 1988, **25**, 75.
11 Littlejohn, D., Lab. Pract., 1987, **36**(10), 126.
12 Frech, W., and Jonsson, S., Spectrochim. Acta, Part B, 1982, **37**, 1021.
13 Lundberg, E., Frech, W., Baxter, D. C., and Cedergren, A., Spectrochim. Acta, Part B, 1988, **43**, 451.

14 Lundberg, E., Frech, W., and Harnly, J. M., *J. Anal. At. Spectrom.*, 1988, **3**, 1115.
15 Carroll, J., Miller-Ihli, N. J., Harnly, J. M., Littlejohn, D., Ottaway, J. M., and O'Haver, T. C., *Analyst*, 1985, **110**, 1153.
16 Littlejohn, D., Cook, S., Durie, D., and Ottaway, J. M., *Spectrochim. Acta, Part B*, 1984, **39**, 295.
17 Koirtyohann, S. R., and Kaiser, M. L., *Anal. Chem.*, 1982, **54**, 1515A.
18 L'vov, B. V., *Spectrochim. Acta, Part B*, 1978, **33**, 153.
19 *CRC Handbook of Chemistry and Physics*, ed. Weast, R. C., CRC Press, Boca Raton, FL, 69th edn., 1988.
20 Holcombe, J. A., *Spectrochim. Acta, Part B*, 1983, **38**, 609.
21 Chaudhry, M. M., and Littlejohn, D., *Analyst*, 1992, **117**, 713.
22 Welz, B., Akman, S., and Schlemmer, G., *J. Anal. At. Spectrom.*, 1987, **2**, 793.
23 Littlejohn, D., Egila, J. N., Gosland, R. M., Kunwar, U. K., Smith, C., and Shan, X.-Q., *Anal. Chim. Acta*, 1991, **250**, 71.