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Reduction of Interference Effects in Flame Atomic Absorption Spectrometry Using Flow Injection Techniques

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Flow injection techniques coupled with flame atomic absorption spectrometry (FI - FAAS) were originally used for

introducing and diluting difficult samples prior to nebulisation. More recently they have been used for fast calibrations and for

modifying samples particularly by the removal of interferences.¹⁻⁴ This has allowed separation procedures, which are often otherwise time consuming and irreproducible, to be carried out rapidly by incorporating various devices into the manifold, such as liquid - liquid extraction chambers,^{5,6} microcolumns of chelating or ion-exchange materials^{4,7-9} and solid gathering filters.¹⁰⁻¹²

Calcium has been determined in several interferent systems by FI - AAS. The interference effect of phosphate has been alleviated, at times completely, by careful adjustment of the operating parameters of the AAS instrument and/or working at low FI pumping rates.^{13,14} The effects of sulphate, molybdate, iodate and arsenate have been removed by isolating calcium as the oxalate at suitable values of pH and temperature.¹⁰ The effects of phosphate and sulphate ions have been removed by using an ion-exchanger.¹⁵ So far, efficient FI separation of calcium from aluminium has not been reported. In this work, a manifold design that affords separation of calcium from aluminium by precipitating basic calcium oxalate is described, such that 10 mg l⁻¹ of calcium was isolated from 200 mg l⁻¹ of aluminium at low pumping rates and at room temperature.

Experimental

Apparatus

The manifold shown schematically in Fig. 1 was constructed from PTFE tubing (i.d. 0.58 mm), a Gilson Minipuls-2 peristaltic pump fitted with PVC pump tubing (i.d. 2.05 mm for acid stream; i.d. 0.04 mm for water and reagent streams). The arms of a four-way rotary valve, Rheodyne 5041, were cut to allow the injection of volumes of less than 50 µl. The Y-connector was home-made from glass having its confluence point blown to approximately 2 ml and packed with chromatographic glass rings (diameter approximately 3 mm). The rings improved mixing and afforded a large surface area for reaction. Precipitates were collected on disposable nylon membrane filters of 0.45 µm pore size and diameters 3, 13 and 25 mm (Gelman syringe filters). A stainless-steel disc, 2 µm pore size, 6 mm filter diameter and 2 mm thickness was also used. Air compensation was achieved with an omnifit T-piece and the pulse dampers were glass T-pieces with their upright arms fitted with 6 cm pump tubes (i.d. 2.79 mm) closed at one end. The spectrometer (Baird Atomic A3400) was optimised for the determination of calcium at maximum sensitivity at 422.7 nm in the air - acetylene flame.

Reagents

Calcium solutions were prepared by diluting stock 1000 mg l⁻¹ solutions (BDH SpectrosoL grade). Aluminium chloride (minimum assay 97%), used as interferent, and the ammonia - ammonium oxalate reagent solutions were prepared from BDH AnalaR grade compounds. The hydrochloric acid (5% V/V), used for dissolving the precipitate, was BDH SpectrosoL

grade. Reagent-grade water, produced by a LiquiPure RG system (reverse osmosis followed by ion exchange), was used for solution make-up and as the carrier stream.

Procedure

The blank or sample was injected, and after 5-min delay the hydrochloric acid stream was switched on to dissolve the precipitate. A three-way rotary valve was positioned in the manifold such that the reagent flowed through the system whilst the acid was diverted and *vice versa*.

Fig. 1. Precipitation manifold: R, 0.05 M NH₃ plus 50 mg l⁻¹ ammonium oxalate monohydrate; Pc, precoil; Ps, damper; a, air-compensation inlet; S, injection point; M, confluence mixer; V, stream-switching valve; Rc, reaction coil (50 cm length, i.d. 0.58 mm); f, filter; [length of tubing (i.d. 0.58 mm) between s and m = 26 cm, between f and AAS = 5 cm]

Results and Discussion

Oxalate precipitation is used for the gravimetric determination of calcium in the presence of various interferences.¹⁶ The analysis has always been time consuming, needing an hour or more for heating the reaction mixture. In this manifold, the ammonia - ammonium oxalate buffer reagent selectively precipitated calcium without heating. Thus, the manifold exhibits one of the advantages of an FI system, *i.e.*, that a reaction does not necessarily have to attain equilibrium to be useful quantitatively.¹⁷

The effects of buffer composition, pumping flow-rate, injected sample volume and temperature on the absorbance peak heights of a 10 mg l⁻¹ calcium solution in different concentrations of aluminium (0-200 mg l⁻¹), when a packed bed of glass beads (length 7.5 cm, i.d. 1.6 mm and mesh size 40-35) is in the manifold, have been discussed elsewhere.¹⁴ The packed bed was able to retain precipitates without excessive pressure build-up in the manifold. A packing of polystyrene granules, however, gave better reproducibility because of its inert hydrophobic surface that allowed precipitate dissolution and subsequent cleaning of the polymer surface to be faster and more efficient than glass beads. The relatively

Table 1. Results for different filters

Filter type	Performance
(1) Nylon membrane, 0.45-µm pore, 5 mm f.d.	0.2 absorbance for 10 mg l ⁻¹ of Ca at 0.3 ml min ⁻¹ , 10:200 Ca: Al tolerated, back pressure excess at 0.3 ml min ⁻¹
Nylon membrane, 0.45-µm pore, 13 mm f.d.	0.18 absorbance for 10 mg l ⁻¹ of Ca at 0.6 ml min ⁻¹ , 10:300 Ca: Al tolerated, back pressure excess at 1 ml min ⁻¹
Nylon membrane, 0.45-µm pore, 24 mm f.d.	0.1 absorbance for 10 mg l ⁻¹ of Ca at 1.5 ml min ⁻¹ , 10:500 Ca: Al tolerated, no back pressure excess but de-gassing at 2 ml min ⁻¹
(2) Stainless steel disc, 2 µm pore, 5 mm f.d.	0.18 absorbance for 10 mg l ⁻¹ of Ca at 1 ml min ⁻¹ , no back pressure excess but de-gassing from 1.5 ml min ⁻¹

lower absorbance obtained with the granules (see Fig. 2) is most likely to be due to a larger dead volume of the packings as a result of the irregular shape of the granules.

Fig. 2. Effect of packed bed material on the absorbance peak of 10 mg l^{-1} of calcium present in aluminium(III) solutions: reagent is $50 \text{ mg l}^{-1} (\text{COONH}_4)_2 \cdot \text{H}_2\text{O}$ in $0.05 \text{ M NH}_4\text{OH}$ at precipitation flow of 1.37 ml min^{-1} and with $38\text{-}\mu\text{l}$ injections. ■, No reagent; □, glass beads; ●, polymer granules

Table 1 shows the performance of the manifold with different filters. The excess pressure build-up in the manifold eventually produced leaks at weak connections. This pressure (gauged by the height of the water level in the dampers) decreased as the filter diameter increased, and as the pumping flow reduced. As the absorbance also decreased, the choice of the 13 mm diameter filter for the analysis of cement and water samples was a compromise. In these experiments the reproducibility of the stainless steel filters was poor compared with that obtained with the nylon membranes.

Table 2. Results for the analysis of cements and water

Sample	Conventional AAS	Conventional AAS + La^{III}	Manifold
Cement 1 (% Ca)	38	47	$50 \pm 1^*$
Cement 2 (% Ca)	36	46	$53 \pm 2^*$
Water ($\text{mg l}^{-1} \text{Ca}$)	78	87	74

* Analyses in duplicate.

Samples of cement and laboratory tap water were analysed for their calcium content by using the manifold. The cement samples were dissolved by the hydrofluoric acid - boric acid method¹⁸ in an ultrasonic bath in 15 min. The water sample was acidified to pH 2 with hydrochloric acid. The solutions were diluted to the linear range of the normal calibration curve for $38 \mu\text{l}$ sample injections (see Fig. 3).

The results for the cement samples obtained by using the manifold are significantly higher than by conventional nebulisation (see Table 2). Further experiments towards improving the linear range of the calibration graph as well as the use of the system for sample pre-concentration are in progress.

The detection limit of 0.25 mg l^{-1} of calcium (three standard deviations) is comparable with that for conventional nebulisa-

Fig. 3. (a). Normal working curves with AAS at 422.7 nm , lamp current 2.2 mA , burner height no. 2.5, C_2H_2 flow 3.5 , air flow 7.5 , impact head and capillary tip position optimised. ■, Conventional AAS; □, conventional AAS + lanthanum(III); ●, manifold with $80\text{-}\mu\text{l}$ injections. (b). Effect of injected sample volume on working curves: ■, $38 \mu\text{l}$; □, $80 \mu\text{l}$; ●, $150 \mu\text{l}$. (c). Recorder tracings of $38 \mu\text{l}$ calcium standards at a precipitation flow of 0.63 ml min^{-1} and dissolution flow of 1.40 ml min^{-1}

tion. A characteristic concentration of 0.32 mg l^{-1} per 0.0044 absorbance at a $38 \mu\text{l}$ injection volume improved to 0.08 mg l^{-1} at $150 \mu\text{l}$, comparable with conventional nebulisation; however, the linear range of the calibration graph decreased with increased injected volume [see Fig. 3(b)]. There is the potential of improving the sensitivity over conventional nebulisation by increasing the injected sample volume and/or increasing the dissolution flow-rate. This improvement can be

achieved by using packed beds rather than membrane filters which, in this manifold, are not amenable to high pumping rates ($>2 \text{ ml min}^{-1}$) because of leakages. The linear range would probably be increased by the use of peak area measurements. A precision of 4% RSD obtained for absorbance peaks at 10 mg l^{-1} of calcium worsened to 15% RSD at 1 mg l^{-1} of calcium. The precision of 2% RSD and 0.1% RSD for the packed bed of glass beads at 10 mg l^{-1} and 1 mg l^{-1} of calcium, respectively, is the best achieved.

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References

1. Wolf, W. R., and Stewart, K. K., *Anal. Chem.*, 1979, **51**, 1201.
2. Tyson, J. F., *Analyst*, 1985, **110**, 419.
3. Růžicka, J., *Fresenius Z. Anal. Chem.*, 1985, **324**, 745.
4. Fang, Z., Xu, S., Wang, X., and Zhang, S., *Anal. Chim. Acta*, 1986, **179**, 325.
5. Sweilch, J. A., and Cantwell, F. F., *Anal. Chem.*, 1985, **57**, 420.
6. Silva, M., Gallego, M., and Valcarcel, M., *Anal. Chim. Acta*, 1986, **179**, 341.
7. Olsen, S., Pessenda, L. C. R., Růžicka, J., and Hansen, E. H., *Analyst*, 1983, **108**, 905.
8. Allen, E. A., Boardman, M. C., and Plunkett, B. A., *Anal. Chim. Acta*, 1987, **196**, 323.
9. Cox, A. G., McLeod, C. W., Miles, D., and Cook, J. J., *J. Anal. At. Spectrom.*, 1987, **2**, 553.
10. Martinez-Jimenez, P., Gallego, M., and Valcarcel, M., *Anal. Chem.*, 1987, **59**, 69.
11. Martinez-Jimenez, P., Gallego, M., and Valcarcel, M., *Anal. Chim. Acta*, 1987, **193**, 127.
12. Martinez-Jimenez, P., Gallego, M., and Valcarcel, M., *Analyst*, 1987, **112**, 1233.
13. Garcia, I. L., O'Grady, C., and Cresser, M., *J. Anal. At. Spectrom.*, 1987, **1**, 221.
14. Adeeyinwo, C. E., and Tyson, J. F., *Anal. Chim. Acta*, 1988, **214**, 339.
15. Kamson, O. F., and Townshend, A., *Anal. Chim. Acta*, 1983, **155**, 253.
16. Erdev, L., in Belcher, R., and Gordon, L., *Editors*, "Gravimetric Analysis II," Pergamon, Oxford, 1965, p. 628.
17. Růžicka, J., *Fresenius Z. Anal. Chem.*, 1988, **329**, 653.
18. Thompson, M., and Wood, S. J., in Cantle, J. E., *Editor*, "Atomic Absorption Spectrometry," Elsevier, Amsterdam, 1982, p. 273.