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Journal of Chromatography A, 673 (1994) 173–179

JOURNAL OF CHROMATOGRAPHY A

Determination of barium and strontium in calcium-containing matrices using high-performance chelation ion chromatography

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(First received February 1st, 1994; revised manuscript received March 17th, 1994)

Abstract

High-performance chelation ion chromatography involving dye-coated resins has been used to determine barium and strontium in samples of mineral water and milk powder containing several orders of magnitude higher levels of calcium and other alkali and alkaline earth metals. Detection limits of 0.03 mg dm^{-3} were achieved for both barium and strontium. The technique was used to determine both metals in a river water certified reference material and all results were compared to inductively coupled plasma optical emission spectroscopy producing overall good agreement between the two methods.

1. Introduction

There is a great deal of interest in the determination of barium and strontium in certain environmental and biological samples. The presence of either or both of the above often occurs in samples containing much larger concentrations of alkali and the other alkaline earth metals, which can cause problems in several commonly used analytical techniques.

When using traditional cation-exchange chromatography magnesium elutes first followed by calcium, strontium and finally barium [1]. Due to the longer retention time barium is often broad and therefore the sensitivity compared to the much sharper calcium and magnesium is greatly reduced. The presence of excess calcium or magnesium in the sample matrix can result in large peaks masking the signal for strontium and barium. Dilution of the sample prior to injection could result in losing the signal for strontium and barium completely. Singh *et al.* [2] illustrated this problem by using a Dionex CS-2 cation-exchange column for the separation and determination of strontium from excess levels of sodium, calcium and magnesium in sub-surface waters. Under the conditions used, strontium eluted last from the column after sodium, calcium and magnesium and gave a broad asymmetrical peak resulting in poor sensitivity.

The determination of barium by other techniques has also given problems. The detection of barium in calcium-containing matrices using atomic absorption spectroscopy has been reported by Jaber and El-Issa [3]. Large interferences were reported due to the CaOH molecular species and solvent extraction to remove the calcium was needed prior to analysis. Jerrow *et al.* [4] illustrated the determination of barium in the presence of large amounts of alkali and alkaline earth metals by direct current plasma atomic emission spectroscopy and showed how

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0021-9673/94/$07.00
SSDI 0021-9673(94)00273-C

magnesium in the sample greatly reduces the interference effects of calcium and strontium. However, they suggest strict guidelines of matrix matching should be followed if reliable results are to be obtained. The analysis of barium in complex matrices using spectrophotometric methods has been studied by Manna *et al.* [5] with Sulphonazo III used as a complexing agent. The presence of both calcium and strontium in wastewaters studied, resulted in major interferences and the method was concluded to be unsuitable for use with such samples.

A relatively new ion chromatography technique developed at Plymouth, high-performance chelation ion chromatography (HPCIC), has been evaluated for the determination of trace amounts of barium and strontium in environmental samples containing high levels of other alkali and alkaline earth metals, particularly calcium. HPCIC essentially involves chelating functional groups immobilised on a HPLC-grade resin. This can be achieved with chelating dyes which are used to impregnate the resin, producing chelating columns that have been shown to exhibit good separation efficiencies [6]. Retention of metal ions is a function of the relative magnitude of conditional stability constants and the order of retention of most groups of metals is found to be the reverse of that using simple cation-exchange chromatography. Therefore, with HPCIC, barium elutes first before strontium, followed by calcium and magnesium. As barium and strontium elute close to the solvent front, HPCIC produces not only very sharp peaks allowing for greater sensitivity for these two metals, but also baseline resolution completely clear of the massive peaks found in samples containing several orders of magnitude higher levels of calcium and magnesium. Salt ions such as sodium and potassium have very little affinity for the chelation sites of the impregnated resin and pass straight through the column. Therefore the ionic strength of the sample has little or no effect upon the separation.

Two samples of current interest were chosen to evaluate the technique. New proposed EC limits [7] for levels of barium in mineral waters of 0.7 mg dm^{-3} require a rapid and sensitive method of analysis. Mineral waters often contain up to 300 mg dm^{-3} calcium combined with high levels of magnesium making the determination of low levels of barium and strontium difficult. The determination of strontium in skimmed milk powder was also carried out as the ratio of strontium to calcium of approximately 1:2000 also causes problems with other techniques.

2. Experimental

2.1. Instrumentation

The HPCIC post-column reaction system used is the same as illustrated by Challenger *et al.* [6]. A LKB 2150 HPLC titanium pump (Bromma, Sweden) was used to deliver the eluent. A Constametric model III pump (Laboratory Data Control, Riviera Beach, FL, USA) was used for post-column reagent (PCR) delivery. Injection of the sample was via a steel six-port injector (Rheodyne, Cotati, CA, USA) connected to a 100-μl PTFE sample loop. Post-column detection was achieved by the mixing of the eluent and the PCR at a zero-dead-volume T-piece followed by a 1.4 m × 0.3 mm I.D. PTFE reaction coil. A spectral array detector (Dionex, Sunnyvale, CA, USA) set at 490 nm was used to detect the eluting metal complexes. A chart recorder (Labdata, Surrey, UK) was used to record the chromatograms.

A Varian Liberty 200 inductively coupled plasma optical emission spectrometry (ICP-OES) system (Melbourne, Australia) was used to compare results with the HPCIC technique. The wavelengths monitored were 407.771 for strontium and 455.403 for barium.

All reagents and samples were stored in acid-washed polypropylene bottles (BDH, Poole, UK).

2.2. Reagents

The reagents used were supplied by BDH except 4-(2-pyridylazo)resorcinol (PAR) and

zinc–ethylenediaminetetraacetic acid (Zn-EDTA) which were obtained from Fluka (Switzerland). Reagents were AnalaR grade unless stated otherwise. All solutions were prepared using distilled and deionised water from a Milli-Q system (Millipore, USA) and degassed using helium before use.

Potassium nitrate (1 *M*) containing 0.05 *M* lactic acid was used as the eluent, adjusted to the correct pH using dilute ammonia or nitric acid. The PCR used was a mixture of $2 \cdot 10^{-4}$ *M* Zn-EDTA, $1.2 \cdot 10^{-4}$ *M* PAR and 2 *M* ammonia. PAR alone is insensitive to alkaline earth metals, by adding Zn-EDTA a displacement reaction occurs [8]. The absorbance measured is due to Zn–PAR which has a $\lambda_{max.}$ of 490 nm. Flow-rates for both eluent and PCR were 1 cm^3 min^{-1}.

Barium and strontium standards were prepared using barium nitrate and strontium nitrate (BDH).

2.3. Chelating column

The production of high-performance chelating columns is based upon the "dye-coating" techniques described by Jones and co-workers [9–12] in several recent papers. Chelating dye-stuffs are permanently immobilised upon HPLC-grade resins resulting in efficient chelating columns with a working lifetime of over 18 months. For the determination of barium and strontium in mineral waters methylthymol blue {3,3′-bis[N,N-di-(carboxymethyl)-aminomethyl]thymol-sulphonephthalein} (Sigma, UK) was used to impregnate 8.8-μm particle size, 120-Å pore size polystyrene–divinylbenzene neutral hydrophobic resin (Dionex). For the determination of strontium in skimmed milk powder phthalein purple (*o*-cresolphthalein - 3′,3″ - bis - methyleneiminodiacetic acid) (Sigma) was used to modify the resin. The resins were impregnated and packed in 10×0.46 cm polyether ether ketone (PEEK) HPLC columns (Alltech, UK).

2.4. Samples

The bottled mineral waters chosen for analysis were used as bought, untreated except for being thoroughly degassed with helium before being injected. The milk powder was ashed in a nickel crucible (1 g) using a Meker burner and dissolved into 10 cm^3 of dilute nitric acid with heating. The solution was neutralised using dilute ammonia and made up to 20 cm^3 immediately before being analysed.

3. Results and discussion

3.1. Choice of chelating column

Investigations into the dye-coating techniques of Jones and co-workers have resulted in the production of several types of high-performance chelating columns using triphenylmethane- or azo-based chelating dyes. The most efficient separations have been achieved using the triphenylmethane group of dyes to which methylthymol blue and phthalein purple belong. Both dyes contain two iminodiacetic acid functional groups which are the active chelating sites of the immobilised molecule. It is interesting to note that when different dyes containing the same functional coordinating group are compared on impregnated resins, significant differences in metal chelating ability are found. However, this is perhaps not too surprising, as small changes in the basicity of the iminodiacetic acid group could have a marked affect on the metal stability constants. The small variations in chelating ability between dyes can be very useful as there is a large number available, allowing chelating columns to be specifically designed for a particular separation. A good example is reported here, where a much greater degree of separation between strontium and calcium was achieved using the phthalein purple column compared to the methylthymol blue column. Therefore, the phthalein purple column was considered more suitable for samples with extremely high levels of calcium and thus used for the determination of strontium in milk powder. Although the order of separation and selectivity factor between metals remains constant for a particular impregnated dye, the conditional stability constant for a particular metal and

hence the speed of elution is markedly affected by pH. Thus, small changes in pH can be used to "fine tune" the separation.

3.2. Barium in mineral waters

Fig. 1 is a chromatogram showing the separation of four alkaline earth metals in 1 *M* KNO_3 at pH 7.9 using the methylthymol blue column. The chromatogram shows sharp peaks for barium and strontium eluting before and completely separate from both calcium and magnesium.

Eight brands of mineral waters were analysed. Three of these contained both barium and strontium and relatively high levels of calcium, so these were chosen for quantitative determinations. These were Evian, Highland Spring and Buxton mineral water. Fig. 2 shows a chromatogram of Highland Spring mineral water, a step down in the pH of the eluent was used after the

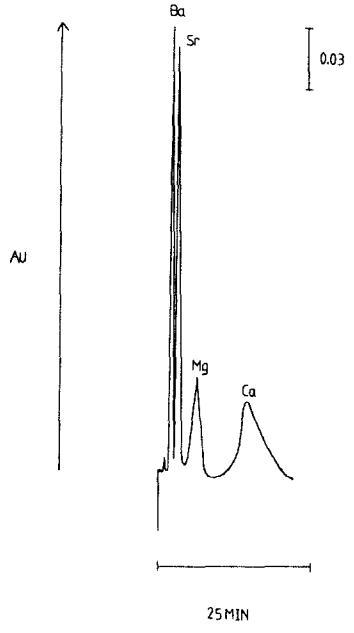

Fig. 1. Chromatogram showing the separation of four alkaline earth metals on a methylthymol blue-impregnated column. Sample: 100-mm^3 injection of 10 mg dm^{-3} barium, strontium, magnesium and calcium. Eluent: 1 *M* KNO_3 with 0.05 *M* lactic acid (pH 7.9). PCR: $2 \cdot 10^{-4}$ *M* Zn-EDTA, $1.2 \cdot 10^{-4}$ *M* PAR and 2 *M* NH_3.

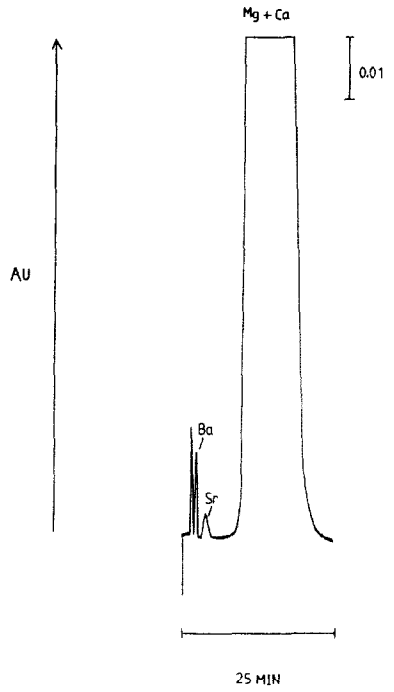

Fig. 2. Chromatogram showing the separation of barium and strontium from magnesium and calcium in Highland Spring mineral water on a methylthymol blue-impregnated column. Sample: 100-mm^3 injection. Eluent: 1 *M* KNO_3 with 0.05 *M* lactic acid (pH 8.5, stepped down to pH 3.0 after 5 min). PCR as in Fig. 1.

elution of barium and strontium to sweep off calcium and magnesium, thus reducing analysis time. Highland Spring contained the highest levels of barium of the samples analysed, approximately half the proposed new limits. Determination of both barium and strontium was obtained through the method of standard additions to take into account any matrix affects which may affect the slope of the calibration graph. Five additions, ranging from 50 to 250 μg dm^{-3} for barium and 100 to 500 μg dm^{-3} for strontium were used. To produce a 500 μg dm^{-3} strontium addition, 100 mm^3 of a 500 mg dm^{-3} strontium standard was added to 100 cm^3 of sample, resulting in negligible dilution of the original sample. Linear calibration curves for both metals were achieved using peak heights. Regression values were $r = 0.999$ for barium and $r = 0.998$ for strontium. The precision of the

method was determined with eight repeat injections of a mixed metal spike of 0.4 mg dm^{-3} barium and 0.8 mg dm^{-3} strontium added to Buxton mineral water containing 50 mg dm^{-3} calcium and 20 mg dm^{-3} magnesium, giving R.S.D. values of 3 and 10%, respectively. Using a 200-mm^3 sample loop detection limits of approximately 0.03 mg dm^{-3} for barium and strontium were achieved, calculated as twice the level of baseline noise. Table 1 shows the results from the analysis of a simulated river water certified reference material IAEA/W-4. Although the levels of calcium and magnesium in the river water, 10 and 4 mg dm^{-3}, were less than those found in mineral waters, the ratios of barium and strontium to calcium was still 1:200. The levels of barium and strontium determined compared well with the certified values. The relatively high R.S.D. values of 20% were a reflection of the fact that levels of both metals were close to the detection limits of the method. Fig. 3 shows a chromatogram of the certified reference material showing peaks for barium and strontium close to the limits of detection. ICP-OES was used to compare with all the results obtained using the HPCIC method. Table 2 compares the two sets of results and shows overall good agreement between the two methods.

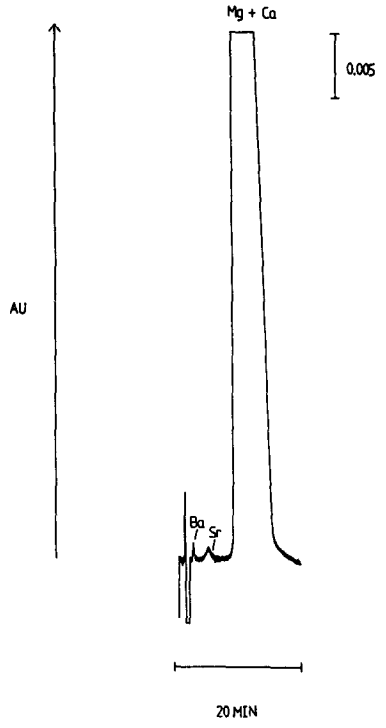

Fig. 3. Chromatogram showing the separation of barium and strontium from magnesium and calcium in fresh river water certified reference material on a methylthymol blue-impregnated column. Sample: 200-mm^3 injection. Eluent as in Fig. 2, PCR as in Fig. 1.

3.3. Strontium in milk powder

Milk powder contains approximately 12 000 mg dm^{-3} calcium and only trace amounts of strontium, resulting in an extremely difficult sample matrix for most methods of analysis. The ashing and acid digestion of 1 g of sample produces a clear digest which was made up to 20 cm^3, resulting in a 20-fold dilution before injections. Fig. 4 shows the separation of barium, strontium and calcium using the phthalein purple column at pH 9.8 in 1 *M* KNO_3. Magnesium is completely retained at this pH. The chromatogram produced from the injection of the milk powder digest is shown in Fig. 5. In practice the calcium and magnesium can be swept off in a much shorter time using an acid wash. However, in this instance, the calcium peak was allowed to run the full time to show that the huge peak

Table 1
Determination of barium and strontium in simulated fresh water IAEA/W-4 certified standard reference material using HPCIC and ICP-OES

Metal ion	HPCIC	ICP-OES	Certified values
Ba(II)	0.05 (0.01)	0.041 (0.002)	0.052 (0.002)
Sr(II)	0.05 (0.01)	0.053 (0.003)	0.050 (0.003)

Values in mg dm^{-3} (±S.D.).

Table 2
Levels of barium and strontium determined in three bottled mineral waters using HPCIC compared with results achieved using ICP-OES

Mineral water	Metal ion	HPCIC	ICP-OES
Evian	Ba(II)	0.09 (0.01)	0.078 (0.003)
	Sr(II)	0.39 (0.01)	0.370 (0.005)
Buxton	Ba(II)	0.11 (0.02)	0.137 (0.015)
	Sr(II)	0.84 (0.07)	0.585 (0.023)
Highland Spring	Ba(II)	0.33 (0.04)	0.364 (0.016)
	Sr(II)	0.25 (0.08)	0.268 (0.010)

Values in mg dm^{-3} (± S.D.).

would cause serious problems with normal ion chromatography, where the order of elution would be reversed. The retention time for the large calcium peak is less than that for calcium shown in Fig. 4. This is due to the massive excess of calcium filling most of the chelation sites at the beginning of the column and thus speeding up the elution of the metal ions. This emphasises the requirement for close matrix matching of standards or standard addition.

For the reasons discussed above, standard addition was used to determine the levels of strontium present in the milk digest. The level of strontium found in the milk powder digest was 0.15 mg dm^{-3} which corresponds to 3.0 mg dm^{-3} in the actual milk powder. Barium was not quantitatively determined as after the 20-fold dilution of the milk powder the level present fell below the working detection limit with a 100-mm^3 sample loop. Linear results were achieved with a regression value of $r = 0.998$. ICP-OES was again used to compare methods, the results of which are shown in Table 3. Good agreement

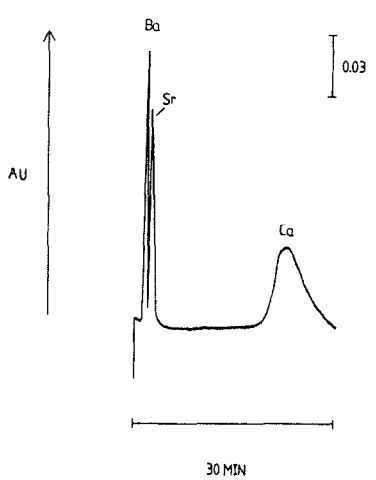

Fig. 4. Chromatogram showing the separation of three alkaline earth metals on a phthalein purple-impregnated column. Sample: 100-mm^3 injection of 5 mg dm^{-3} barium and strontium and 10 mg dm^{-3} calcium. Eluent: 1 *M* KNO_3 with 0.05 *M* lactic acid (pH 9.8). PCR as in Fig. 1.

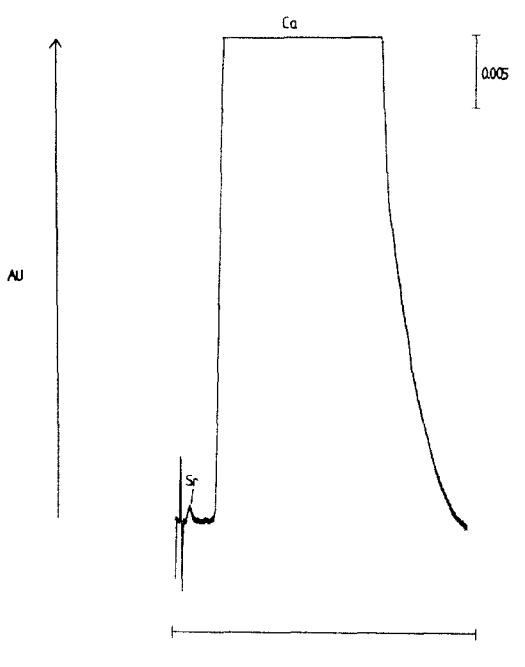

Fig. 5. Chromatogram showing the separation of strontium from calcium in milk powder digest on a phthalein purple-impregnated column. Sample: 100-mm^3 injection. Eluent: 1 *M* KNO_3 with 0.05 *M* lactic acid (pH 10.2). PCR as in Fig. 1.

Table 3
Determination of strontium in milk powder digest using HPCIC compared with results achieved using ICP-OES

Metal ion	HPCIC	ICP-OES
Ba(II)	ND[a]	0.027 (0.002)
Sr(II)	0.15 (0.03)	0.125 (0.005)

Values in mg dm^{-3} (± S.D.).
[a] Below detection limit.

between the two methods was achieved, although the R.S.D. value for the chelation ion chromatography method was higher than those for ICP-OES, again reflecting the closeness of the signal to the detection limit in HPCIC compared to ICP-OES.

4. Conclusions

The HPCIC technique as outlined in this paper provides a quick and inexpensive solution to the determination of both barium and strontium in calcium- and magnesium-containing matrices. The results achieved for mineral waters and milk powder compared well with ICP-OES. The production of chelating columns is relatively simple and there is a large number of chelating dyes available to produce a range of separation characteristics, the most suitable of which can be chosen to suit a particular sample. The system can also be readily adapted to run as a on-line monitoring system and clearly will serve as a useful alternative to atomic spectrophotometric techniques.

Acknowledgements

The authors wish to thank the Science and Engineering Research Council (SERC) for financial support and Dionex (UK) Ltd. for sponsorship through the CASE award scheme.

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