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High-performance chelation ion chromatography for the determination of traces of bismuth in lead by means of a novel hypercrosslinked polystyrene resin

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Abstract

A method for the determination of trace bismuth in lead using a high-performance chelating ion chromatography (HPCIC) system is described. A novel high-efficiency chelating column was prepared from a neutral hypercrosslinked polystyrene resin, MN200 (Purolite). It was found that the unmodified material had metal complexing properties similar to resins containing immobilized chelating dyestuffs. The resin was very stable in strong acid conditions and was therefore suitable for the investigation of metal ions with high positive charge. Bismuth was eluted with good peak shapes using halogen acids. Hydrobromic acid was chosen as it gave more sensitive detection than hydrochloric acid. Detection was carried out by direct UV–Vis absorption measurement of the bismuth bromide complex so no post-column reaction system was required. No interference was observed from lead halides at 370 nm. A certified lead reference material (CRM 288B) was used to successfully validate the method. The detection limit for bismuth was found to be $10 \mu\text{g l}^{-1}$ and analysis times were less than 5 min from the time of injection. © 1997 Elsevier Science B.V.

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1. Introduction

The determination of certain trace metals in complex matrices can present problems for the analytical chemist in terms of attaining the required limits of detection in the presence of major interferences. The problem is particularly difficult when the matrix contains massive amounts of major metals. A good example of this is the requirement for the determination of bismuth in lead. In this instance some analytical methods require the removal of the lead matrix prior to the bismuth analysis. Suzuki et

al. [1] reported the determination of bismuth in lead shotgun pellets using inductively coupled plasma (ICP)-MS where the lead matrix was eliminated as a lead sulphate precipitate in order to avoid isobaric interferences. This approach, however, can be time consuming and there is a possibility of entrainment effects, resulting in poor analytical recovery. A classical spectrophotometric method has also been described for the determination of bismuth in lead as an iodide complex, but again the matrix is removed before the analysis to prevent formation of a heavy precipitate of lead iodide [2]. Another method for the determination of bismuth has arisen because of the need to study bismuth in lead–lithium alloys. These

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alloys are stated for use in the production of tritium by neutron bombardment in future nuclear fusion plants. Bismuth contamination of these alloys may result in the formation of undesirable radioactive polonium isotopes during this process and there is therefore a need to monitor bismuth concentrations at frequent intervals. Judex et al. [3] developed a stripping voltammetric method for this study. In the method described, the lead matrix appears to have no effect on the bismuth determination but copper present in concentrations of greater than 140 times causes significant interference.

High-performance chelation ion chromatography (HPCIC) offers an alternative approach for the determination of bismuth in lead. Whereas simple ion-exchange columns could be 'swamped' by the lead matrix leaving no capacity to analyse the bismuth, chelating ion exchange has the potential to separate one or two metal ions from much greater concentrations of other metals.

Previous research at the University of Plymouth has involved the preparation of high-performance chelating columns suitable for operation in high ionic strength media. Small particle size polystyrene resins have been impregnated with chelating dyes and 'permanent' chelating surfaces have been achieved after removing loosely associated dye from the columns. A series of different azo- and triphenyl-methane-based dyes have been impregnated into the polystyrene resins in order to prepare columns with variations in selectivity and metal-retaining capacity [4]. These chelating ion-exchange columns have been successfully employed for both the separation and determination of trace metals from high-metal-containing matrices such as sea-water [5], oil-well brines [6], mineral waters and milk powder [7] in single-column systems.

This study involves the preparation of novel chelating ion exchange from a neutral hypercross-linked polystyrene resin (Purolite MN200). In this case, however, the identification of interesting inherent chelating properties meant that further modification of the resin, using chelating dyes, was not required. MN200 is a high surface area polymer (1000–1500 m²/g) and owing to the high level of crosslinking (40–60%), it can be easily crushed, maintaining a rigid structure suitable for producing closely packed columns. This investigation reports

the application of a small particle size MN200 column for the direct determination of bismuth in lead after acid dissolution.

2. Experimental

2.1. Instrumentation

A Dionex GP40 inert gradient pump (Dionex, Sunnyvale, CA, USA) was used to deliver the mobile phase. A Rheodyne 9010 six-port injector (Rheodyne, Cotati, USA) was used to inject the samples via a 100- μ l sample loop. The analytical column was a polyether ether ketone (PEEK) (50 \times 4.6 mm I.D.) casing packed with Purolite MN200 (crushed to a mean particle size of 20 μ m). A Spectral Array Detector (Dionex) was used, set at 370 nm.

2.2. Reagents

Hydrobromic acid (48%) (Aldrich, Milwaukee, WI, USA) was used to prepare the eluent at various concentrations by simple dilution with distilled and de-ionised water from a Milli-Q (Millipore, USA) water purification system. Bismuth standards were prepared in 0.1 M 'AnalaR' nitric acid (BDH, Poole, UK) by serial dilution of a commercially produced 1000 μ g ml⁻¹ bismuth nitrate standard (BDH).

2.3. Preparation of small particle size MN200

The MN200 was crushed and fractionated using fine mesh sieves. The mean particle size was measured using a Malvern Mastersizer 2.1 (Malvern Instruments, Malvern, UK).

2.4. Sample preparation

Lead pellets (1 g) (CRM 288B, BAS) were dissolved in 10 ml of 12.5 M nitric acid on a hotplate and diluted to 50 ml. Aliquots of the solution (10 ml) were diluted further to 100 ml with concentrations of 0.5, 1.0 and 1.5 μ g ml⁻¹ of bismuth added, respectively, to three of the four samples for a standard additions method.

3. Results and discussion

3.1. Preliminary studies

The MN200 hypercrosslinked resin was originally chosen for investigation owing to the manufacturer's claim that it could adsorb fairly high concentrations of organic compounds from aqueous media. Thus, it appeared to be suitable for current research on immobilising chelating dyes for the purpose of trace metal analysis. Preliminary research showed that although MN200 was suitable for adsorbing organic chelating dyes it was found that the untreated resin surface had inherent metal ion-adsorbing properties which could also be exploited. The exact nature of the metal ion adsorption was not known and further investigation of the properties of MN200 were required. This was achieved by preparing a 15-cm column of 20 μm MN200 and attempting a separation of a metal mixture using an ion chromatography system.

A 100- μl injection of a zinc, cadmium and lead sample, using a 0.5 M potassium nitrate eluent at pH 4.4, produced a separation typical of a substrate with an immobilised O,O-type chelating group (Fig. 1). The presence of a high concentration of potassium nitrate ruled out any possibility of simple cation or anion exchange occurring. It could be possible that some of the polystyrene backbone was modified during manufacture causing the formation of chelating groups. The above study was repeated 6 months later on a completely new batch of MN200 with very similar results, showing it was not a spurious effect of one particular batch. Our findings are also supported by the workers who helped pioneer the development of this type of hypercrosslinked resin. They recently reported unusual metal-adsorbing properties of this substrate and postulated complex formation of metal ions with organic moieties from benzene rings in the polystyrene resin [8]. Further investigations with the resin showed that the chelating properties did not degrade in the presence of high acid strength media and that MN200 could be utilised for the separation of highly valent metal ions which are hydrolysed at low pH values. Thus, the MN200 chelating column was found to be particularly suitable for the determination of bismuth in lead. In high acid strength media, the MN200

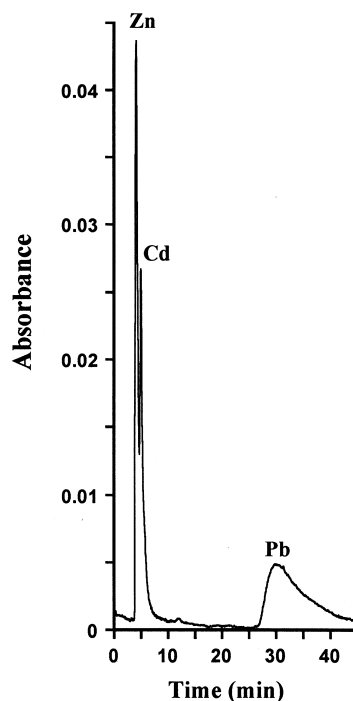


Fig. 1. A 100- μl injection of 5 mg l^{-1} Zn^{2+} , 20 mg l^{-1} Cd^{2+} and 20 mg l^{-1} Pb^{2+} . The eluent was 0.5 M KNO_3 –0.05 M lactic acid adjusted to pH 4.4 with NH_3 . A 15-cm unmodified 20- μm MN200 column was used and post column detection was with PAR at 490 nm.

columns are capable of retaining bismuth ions and have little affinity for the lead matrix ions, which elute on the solvent front. In addition, by using a hydrobromic acid eluent, bromide complexes of bismuth are formed which can then be detected in the near UV region with no interference from the lead. This eliminates the need for a second pump to deliver a post-column reagent and also saves time in reagent preparations. In effect, although there is a separation of bismuth from the lead matrix, any tailing of the lead peak does not interfere with the determination of bismuth since the detection system is very specific for bismuth.

3.2. Optimisation of separation and detection performance

Initial investigations confirmed that the sensitivity of the bismuth–bromide complex increased slightly with increasing concentrations of the hydrobromic

acid eluent. Also, an increase in the hydrobromic acid concentration resulted in a decrease in the bismuth retention time. For example, 0.5 M HBr gave a retention time of 10 min and 2 M HBr gave a retention time of 1.5 min. A concentration of HBr was required, producing good sensitivity, while giving a Bi peak not too close to the solvent front. A hydrobromic acid concentration of 1.8 M was found to give the best compromise in this regard. A range of bismuth standards from $40 \mu\text{g l}^{-1}$ to 2mg l^{-1} were prepared and 100- μl injections were made to test the linearity of the detection system. The eluent was 1.8 M HBr with detection at 370 nm. Fig. 2 displays the chromatogram for a 100- μl injection of $200 \mu\text{g l}^{-1}$ Bi. The standards were injected twice and a calibration curve was plotted from the peak areas. The correlation coefficient, $r=0.99991$ for the calibration indicated that the system was linear up to 2mg l^{-1} . The equation for the line was, $y=25.90x - 0.124$, the y values being in relative integrator units.

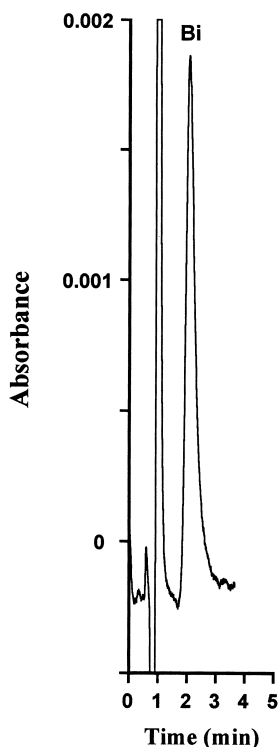


Fig. 2. A 100- μl injection of $200 \mu\text{g l}^{-1}$ bismuth into a 5-cm, 20- μm MN200 column. The eluent was 1.8 M HBr, and detection was at 370 nm.

Since nitric acid was to be used to digest the lead samples, it was also used as an experimental blank for the system. UV-Vis spectrophotometric analysis of nitric acid indicated that there was no absorption above 350 nm. It was found that when using the 1.8 M HBr eluent, with detection at 370 nm, there was no change in signal at the same retention time for a Bi peak when a 100- μl injection of 0.1 M nitric acid was made.

3.3. Analysis of a lead reference material

A certified reference material (CRM 288B, lead pellets) containing Bi was used to evaluate the validity of this method. Standard addition techniques were used throughout this application to account for any matrix interferences which could affect the slope of the calibrations. Approximately 1 g of pellets was used, diluted to 500 ml, for each Bi standard addition calibration. Additions of 0.5, 1.0 and 1.5 mg l^{-1} Bi were added to the respective lead solutions for each determination and 100- μl injections were made into the system. Fig. 3 shows a 100- μl injection of one of the samples with a 1-mg l^{-1} Bi addition. Three separate standard addition calibrations, A, B and C, were carried out on three separate 1-g lots of the lead reference material. The three standard calibration curves were all very similar. For example the correlation coefficient, r , for calibration B was 0.99996 and the equation for the line was, $y=26.13x+11.41$. The numerical values are the same relative integrator units as the previous calibration and the intercept value was used to calculate the concentration of bismuth in the standard sample.

Table 1 displays the information for the three separate analyses. The mean concentration of Bi determined in the CRM 288B lead pellet samples by HPCIC was $218.3 \pm 0.98 \mu\text{g g}^{-1}$ compared to the certified value of $215.8 \pm 5.3 \mu\text{g g}^{-1}$. The HPCIC mean was slightly higher than the certified result, but well within one standard deviation. According to the BCR certificate an analytical method is said to perform well if the mean is within two standard deviations of the certified value. Thus, the HPCIC system is shown to be a valid method for the determination of Bi in lead.

The reproducibility of the system was also investi-

Table 1
Comparison of HPCIC and certified results for bismuth in lead

Lead sample	Amount of Bi determined in the sample ($\mu\text{g g}^{-1}$)	<i>r</i>
A	218.56	0.99927
B	217.26	0.99996
C	219.18	0.99987

Mean result for this work (± 1 S.D.) = 218.3 (± 0.98) $\mu\text{g g}^{-1}$. Certified result for CRM 288B (± 1 S.D.) = 215.8 (± 5.3) $\mu\text{g g}^{-1}$.

gated, with six repeat 100- μl injections of a 1.0 mg l^{-1} Bi standard yielding a R.S.D. of 1.5%. This very good precision is a reflection of the high stability and reproducibility of the chromatographic system. The limit of detection, obtained by calculating three times the signal-to-noise ratio for a 100- μl injection of Bi, was found to be 10 $\mu\text{g l}^{-1}$. This may be further improved by adjusting the sample injection volume, flow-rate, HBr concentration and the column length, until optimum conditions are obtained. A higher efficiency column, achieved by reducing the particle size and range of the packing material, will also

improve system performance. Another important feature of the system was the sample throughput, with each analysis taking less than 5 min from the time of injection. There was no indication of deterioration of the column after 2 months operation with strongly acidic HBr solutions, indicating that the hypercrosslinked MN200 matrix was very resistant to strong acids.

4. Conclusions

A HPCIC system was successfully developed for the determination of bismuth in lead using a novel high-performance chelating ion-exchange column. The column was prepared from a neutral hypercrosslinked polystyrene resin with unexpected chelating properties. Although the exact nature of the metal-complexing function is not known, the polymer was stable in high acidities, giving a good analytical performance as shown by the determination of bismuth in the certified lead sample. The direct UV-Vis absorption measurement of the bromide complex gave a reasonably low detection limit. This could be further reduced by using a smaller particle size resin. A number of other acid hydrolysable metals show strong UV-Vis absorption as their halide complexes and further studies are under way to investigate the full potential of this interesting resin.

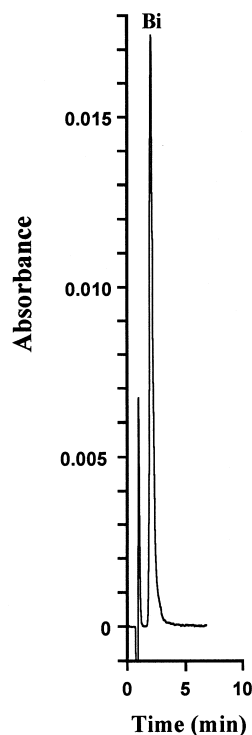


Fig. 3. A 100- μl injection of lead sample A with 1.0 mg l^{-1} Bi added, chromatographed on a 5-cm MN200 column. The eluent was 1.8 M HBr, with detection at 370 nm.

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