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DEVELOPMENT OF HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY METHODS FOR TRACE METAL ANALYSIS

DETERMINATION OF TRACE COBALT IN SIMULATED PRESSURIZED WATER REACTOR PRIMARY COOLANT

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SUMMARY

A high-performance liquid chromatographic system was developed to determine trace metals in simulated Pressurized Water Reactor primary coolant. Cobalt is the main species of interest in this report and an on-line preconcentration column was used to increase sensitivity. Separation was achieved using an Aminex A9 analytical column and a mobile phase containing tartaric acid. Detection was by post-column reaction with eriochrome black T and up to ten metal species could be separated using this system. Good linear calibrations were obtained from 2.5–100 ng of cobalt absolute weight, using volumes up to 200 ml. The detection limit for a 200-ml sample was 0.01 ng ml⁻¹.

INTRODUCTION

The application of high-performance liquid chromatography (HPLC) for rapid, multi-element trace analysis, has increased steadily in the past ten years, with a number of separation and detection methods having been developed¹⁻⁴. One of the major advantages of HPLC is its potential for on-line and automated analysis of streams and circuits in a variety of industrial processes. It was considered that an HPLC system could be ideal for the monitoring of trace metal species in the primary coolant of a pressurized water reactor (PWR). Such an HPLC system would not only allow continuous on-line monitoring of chemical and physical transients, but also reduce the problem of adventitious sample contamination associated with discrete sampling methods. A further advantage is the multi-element capability which would help to keep the number of analytical techniques required to a minimum.

The ratio of metal alloys in contact with the primary coolant, in terms of surface area, is *ca.* 75% Inconel, 20% Zircalloy and 5% stainless steel. The influence of PWR circuit chemistry conditions on the release and deposition of corrosion products species such as manganese, iron, cobalt and nickel, has to be studied and optimized to minimize out-of-core radiation fields. There is particular interest in ⁵⁹Co

since it is the precursor of ^{60}Co , the predominant activation product found in circuit deposits. Reducing out-of-core activity is important as it minimizes maintenance costs and therefore assists in the economic viability of the plant.

A number of difficulties have been experienced in the analysis of the coolant by currently available techniques. These arise from a combination of very low elemental concentrations [$0.01\text{--}1.0\text{ ng ml}^{-1}$ (ppb)] and interferences caused by lithium and borate ions present in the coolant. At present the determination of manganese, iron, cobalt and nickel is carried out by either the lengthy preconcentration onto ion-exchange filters followed by X-ray fluorescence and/or electrothermal atomic absorption spectroscopy. Recently differential pulse polarography (DPP)⁵ and differential pulse stripping voltammetry⁶ have been proposed as alternative methods of analysis, with detection limits in the order of $0.01\text{--}1.0\text{ ng ml}^{-1}$, for nickel and cobalt; however, such methods cannot be readily adapted to on-line automation.

Electrochemical⁴ and photometric¹ measurement of metal complexes are the two main detection systems currently used in the inorganic application of HPLC, with reported detection limits in the range $0.1\text{--}1.0\text{ ng ml}^{-1}$. In order to achieve limits in the pg ml^{-1} range, a number of approaches have been adopted, namely: the use of large injection volumes⁷, new detector designs⁸ and the use of fluorescent⁹ and radiochemical¹⁰ detection systems. Sample preconcentration, either directly onto the chromatography column¹¹ or onto a precolumn¹², offers the most versatile approach to ultra-trace analysis.

This paper describes the development of an HPLC method for the analysis of trace metal species in both simulated PWR primary coolant and distilled deionised water samples, with particular reference to the analysis of cobalt at the pg ml^{-1} level.

EXPERIMENTAL

Apparatus

The liquid chromatographic system (Fig. 1) consisted of a high-pressure stainless-steel eluent pump (Constametric III; Laboratory Data Control (LDC), Riviera Beach, FL, U.S.A.) and a high-pressure stainless-steel reagent pump (Model AA dual-piston Eldex pump; Eldex Labs., Mento Park, CA, U.S.A.). Sample enrichment was carried out with a high-pressure PTFE-lined sample plump (Model AA dual-piston Eldex pump), connected to a Model 7010 Rheodyne injector valve (Rheodyne, Cotati, CA, U.S.A.) fitted with a preconcentration column. The detector was a double beam UV-visible spectrophotometer (SF770; Shoefel, Westwood, NJ, U.S.A.), and the 1 cm length flow-cell of $10\ \mu\text{l}$ capacity was monitored at 610 nm. The LDC pump, the data from the spectrophotometer and the printer (Houston Model, LDC) were controlled by a central microprocessor control unit (Control Command Module, LDC).

The analytical column was maintained at 60°C by immersion in a Grant-type JB1 water-bath (Grant Instrumentation, Cambridge, U.K.). The conditions used throughout were an eluent flow-rate of 1.5 ml min^{-1} , a post-column reagent flow-rate of 1.0 ml min^{-1} , and a PTFE post-column reaction coil of 0.6 ml.

Materials and reagents

Distilled deionised water (DDW) was used throughout, with all samples, stan-

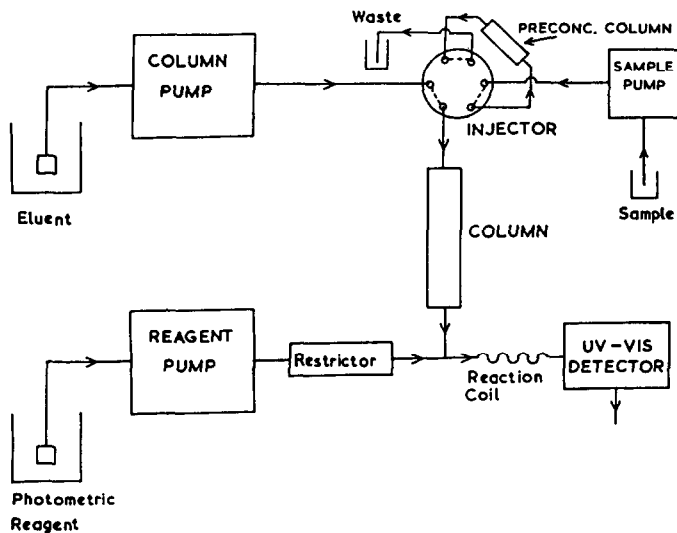


Fig. 1. Schematic diagram of apparatus.

dards and reagents being stored in polyethylene bottles, which had previously been contacted with IM Aristar-grade nitric acid for 16 h, followed by five separate washings with DDW. Whenever possible Aristar grade chemicals (BDH, Poole, U.K.) were used.

Standards were prepared by sequential dilution from 1000 ppm stock solutions. A stock solution of eriochrome black T (EBT) reagent (4 g l^{-1}), in 2 M ammonia was prepared, from which the following daily working solution was prepared: EBT-DDW- 2 M ammonia (4:296:200). The lithium borate solution (LBS), contained 1200 mg l^{-1} of borate (typical of a PWR primary coolant), adjusted to pH 6.5 with 1.8 mg l^{-1} lithium hydroxide.

The cation-exchange resin (Aminex A9, $11.0 \pm 0.5 \mu\text{m}$, Bio-Rad) was slurry-packed at 3500 p.s.i. into both the $100 \text{ mm} \times 4.6 \text{ mm}$ I.D. stainless-steel analytical column and the $50 \text{ mm} \times 4.6 \text{ mm}$ I.D. titanium preconcentration column.

Preliminary considerations

Selection of the column material was based upon the requirement to operate over a long period of time. Therefore the cation-exchange resin (Aminex A9) was chosen because of its known long-term stability^{3,12}. This necessitated the selection of a more strongly chelating polycarboxylic acid, and tartaric acid was used as eluent^{3,12}. The detection system was the EBT inverse photometric method described in detail elsewhere¹³, having an absolute detection limit for $100\text{-}\mu\text{l}$ injection of *ca.* 1 ng for Ni^{2+} , Co^{2+} , Mn^{2+} and Fe^{2+} . Consequently to achieve the desired detection limit of 10 pg ml^{-1} , sample preconcentration was required. Techniques such as solvent extraction and sample evaporation are not particularly suitable for this application because they are generally time-consuming and cannot readily be automated for on-line analysis. Direct preconcentration onto an analytical column requires a longer analysis time per sample, is less flexible in operation and does not offer the

facility for guarding the analytical column from contamination. Preconcentration of the sample was achieved by collecting a known volume of sample onto a 50 mm × 4.6 mm I.D. titanium precolumn, packed with Aminex A9. The preconcentrated sample was backflushed off the precolumn using 0.2 M tartaric acid onto an Aminex A9 stainless-steel analytical column (100 mm × 4.6 mm I.D.). After 90 s the Rheodyne injector was switched back into the load position, enabling another sample to be concentrated, while the first was being analysed. To illustrate the capability of the separation system for the determination of the metals of interest, a typical chromatogram is shown in Fig. 2.

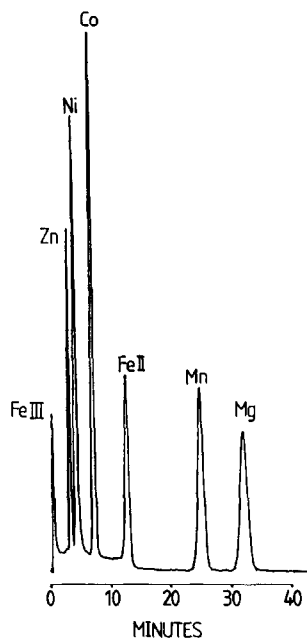


Fig. 2. Separation of mixed metal standard (100- μ l injection). Metal ion concentrations: 5 ppm Fe^{3+} , Zn^{2+} , Ni^{2+} , and Mn^{2+} ; 10 ppm Mg^{2+} ; and 25 ppm Fe^{2+} . Chromatographic conditions: 100 × 4.6 mm I.D. Aminex A9 column; eluent, 0.2 M tartaric acid (pH 4.3) at 1.5 ml min^{-1} ; detection, post-column reaction with $7 \cdot 10^{-5}$ M EBT solution pumped at 1.0 ml min^{-1} ; wavelength 610 nm.

RESULTS AND DISCUSSION

Prior to the investigation into the effectiveness of the preconcentration system, it was necessary to examine the stability of extremely low concentration of metal ions in different solutions. This was assessed by measuring the peak height response for 10 ml of a 10 ppb mixed metal solution. Four different aqueous systems were investigated and preconcentration volumes were chosen to give a calibration graph for each metal over a 20–100 ng weight range.

The four aqueous systems were: (i) DDW; (ii) 0.0014 M nitric acid; (iii) 0.001 M citrate buffer; and (iv) simulated primary coolant (LBS).

The peak height response for cobalt was similar for all four aqueous systems; however, on standing 24 h, a repeat analysis showed a decrease in the peak height response for standards made up in DDW. Cassidy and Elchuk¹² also studied the stability of standards at trace levels and reported a similar effect for nitric acid solutions after 100 h. The work reported here was only carried out over a 24-h period, and showed no decrease for standards prepared in nitric acid. However, higher blanks for nickel and iron were obtained, presumably due to the greater ability of the nitric acid to leach metals from wetted components. Consequently control standards were prepared and stabilized in 0.001 M citrate buffer and compared with spiked solutions of simulated primary coolant water (LBS) in subsequent work.

Investigation of preconcentration system

The effectiveness of the preconcentration system for the determination of cobalt at the required concentration was investigated by considering the following criteria: (a) system contamination; (b) reproducibility of analysis; (c) quantitative performance of the preconcentration column; (d) stability of very low concentrations (ng ml^{-1}) of metal ions; (e) detection limit for large preconcentration volumes.

(a) Contamination is one of the major problems of ultra-trace analysis. When considering the effects of contamination on the system described here it is best treated as two separate units, the preconcentration section and the separation section. The separation section (the pumps connecting tubing and analytical column) is composed entirely of stainless-steel components. The tartrate eluent flows continuously and any metal leached from the stainless-steel surfaces will reach a steady state producing a constant background. However, leaching is best kept to a minimum otherwise too much of the EBT reagent will be consumed. Thus the metal frits in the analytical column, which have a very high surface area, were replaced with PTFE frits. The situation regarding the preconcentration section is very different. Any metals leached from the wetted components will build up on the preconcentration column. Since preconcentration volumes can be 200 ml or more, leaching of metals could result in significant contamination. To reduce this contamination, PTFE tubing was used for all connections, the Eldex sample pump was PTFE lined, and the preconcentration column was made of titanium with PTFE frits as bed supports. The only remaining stainless steel in the preconcentration system was the small amount in the inlet and outlet ports of the Rheodyne valve. Some contamination will still be present mainly from the reagents and deionized water. This will build up on the preconcentration column when a sample is preconcentrated affecting blank levels and thus the limit of detection. This will be discussed in section (e).

(b) The reproducibility of analysis, at both the 1 ng ml^{-1} and the 10 ng ml^{-1} levels, was determined for freshly prepared standards throughout a working day. In each case a total weight of 50 ng was preconcentrated for each determination. Table I shows the statistical interpretation of these results. The results show good reproducibility throughout a working day, and are an indication that there were no adsorption losses, even for a 1 ng ml^{-1} LBS standard.

(c) In order to investigate the quantitative response of the preconcentration column, different concentrations of cobalt in differing volumes of both LBS and citrate stabilised standard solutions were analysed. The results are shown in Table II. The absolute amounts of cobalt preconcentrated vary from 2.5 to 100 ng. The

TABLE I
REPRODUCIBILITY OF PRECONCENTRATED SAMPLES

	<i>Citrate solutions</i>		<i>LBS solutions</i>	
	<i>10 ng ml⁻¹</i>	<i>1 ng ml⁻¹</i>	<i>10 ng ml⁻¹</i>	<i>1 ng ml⁻¹</i>
Number of replicate analyses	6	8	6	8
Standard deviation	2.52	1.17	2.62	6.25
Coefficient of variation (%)	3.8	2.2	4.9	6.4

TABLE II
QUANTITATIVE RESPONSE OF PRECONCENTRATION COLUMN

	<i>Volume concentrated (ml)</i>	<i>Concentration (ng ml⁻¹)</i>	<i>Weight concentrated (ng)</i>	<i>Corrected peak height</i>	<i>Normalized* peak height</i>
Lithium borate solutions	100	1	100	182	182
	54	1	54	86	159
	25	1	25	39	156
	190	0.1	19	34	179
	100	0.1	10	17	170
	50	0.01	5	8.5	170
	25	0.1	2.5	3.75	150
Citrate stabilized solutions	10	10	100	146	146
	5	10	50	71	142
	25	1	25	39	156
	10	1	10	14	140
	200	0.1	20	28	140
	100	0.1	10	14	140
	25	0.1	2.5	4	160

* Peak height has been normalized to give value for 100 ng of cobalt preconcentrated.

normalized figures show the response is very consistent, indicating good linearity of preconcentration over a wide range of volumes and concentrations (absolute weight range 2.5–100 ng). The minimum levels of cobalt in a PWR primary coolant may be very low (0.01 ng ml⁻¹), thus preconcentrated samples will have small absolute weights concentrated. Therefore a further set of calibration graphs for both LBS and citrate stabilized solutions were produced to assess the linearity of preconcentration of different volumes of 0.1 ng ml⁻¹ solutions over an absolute weight range of 2.5–20 ng (Fig. 3). Both graphs show a good linear response for the preconcentration of large volumes of dilute concentrations of cobalt in both LBS and citrate stabilised solution.

(d) Following the initial investigation of the stability of these very low concentrations of metal ions in solution, a long term stability trial was set up, to measure the stability of solutions at both the 1 ng ml⁻¹ and the 10 ng ml⁻¹ concentrations.

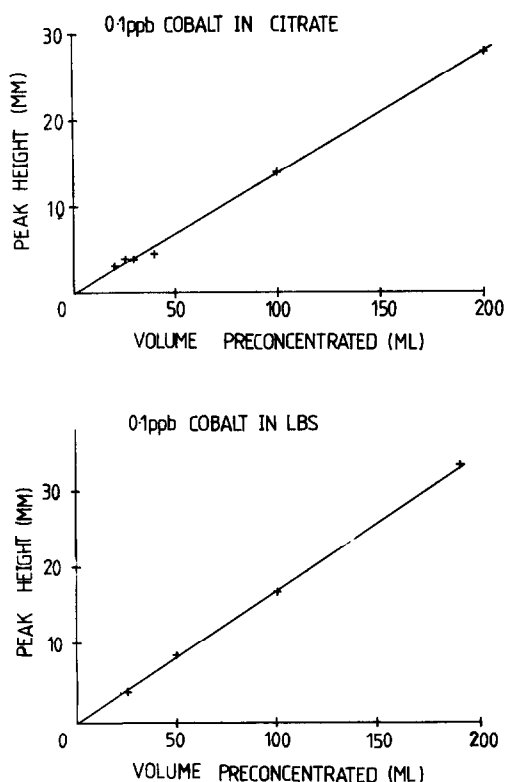


Fig. 3. Calibration graphs for blank corrected peak height response against volume preconcentrated.

In each trial 50 ng of cobalt were preconcentrated and the cobalt peak height of the aged sample was divided by the cobalt peak height of a freshly prepared standard and plotted against time, thus allowing for any variation in peak height response arising from daily preparation of eluent and post column reagent. For the 10 ng ml^{-1} and the 1 ng ml^{-1} concentrations the ratios were measured over nine days and eight days respectively. Statistical variation of these ratios against time is shown in Table III. The results demonstrate good stability of metal ion solutions at the 10 ng ml^{-1} level over a nine-day period, in citrate-stabilized solutions as well as in LBS.

TABLE III

STABILITY TRIAL OF COBALT STANDARD SOLUTIONS

	<i>Citrate solutions</i>		<i>LBS solutions</i>	
	10 ng ml^{-1}	1 ng ml^{-1}	10 ng ml^{-1}	1 ng ml^{-1}
Mean ratio	1.024	0.973	1.001	0.823
Standard deviation	0.069	0.039	0.085	0.174
Coefficient of variation (%)	6.8	4.0	8.5	21.1

However at the 1 ng ml^{-1} level over an eight-day period, the LBS was less stable, giving a coefficient of variation of 21.1%. The citrate-stabilized solution shows better long-term stability at very low concentrations and is therefore considered more suitable for making up reference standards.

(e) To assess the detection limit, large volumes of spiked samples and blanks were preconcentrated and analysed. Results are shown in Figs. 4 and 5. From Fig. 4, the detection limit for cobalt (twice the peak-to-peak baseline noise) in a 190-ml preconcentrated sample of simulated PWR primary coolant, is *ca.* 10 pg ml^{-1} . This clearly shows the ability of the system to achieve the desired limit of detection in the solution matrix of a PWR primary coolant. Contamination from boric acid was particularly noticeable for cobalt and magnesium and to a lesser extent zinc, since a 200-ml citrate reagent blank (Fig. 5) gave much lower peak heights for these metals, the cobalt peak height being reduced by a factor of six. Iron levels were lower in LBS than citrate probably owing to the greater ability of citrate solution to leach metals from the small amount of 316 stainless-steel wetted components. For nickel and iron the levels of contamination are at present acceptable because the expected levels in a primary coolant are two to three orders of magnitude higher than those in the blank.

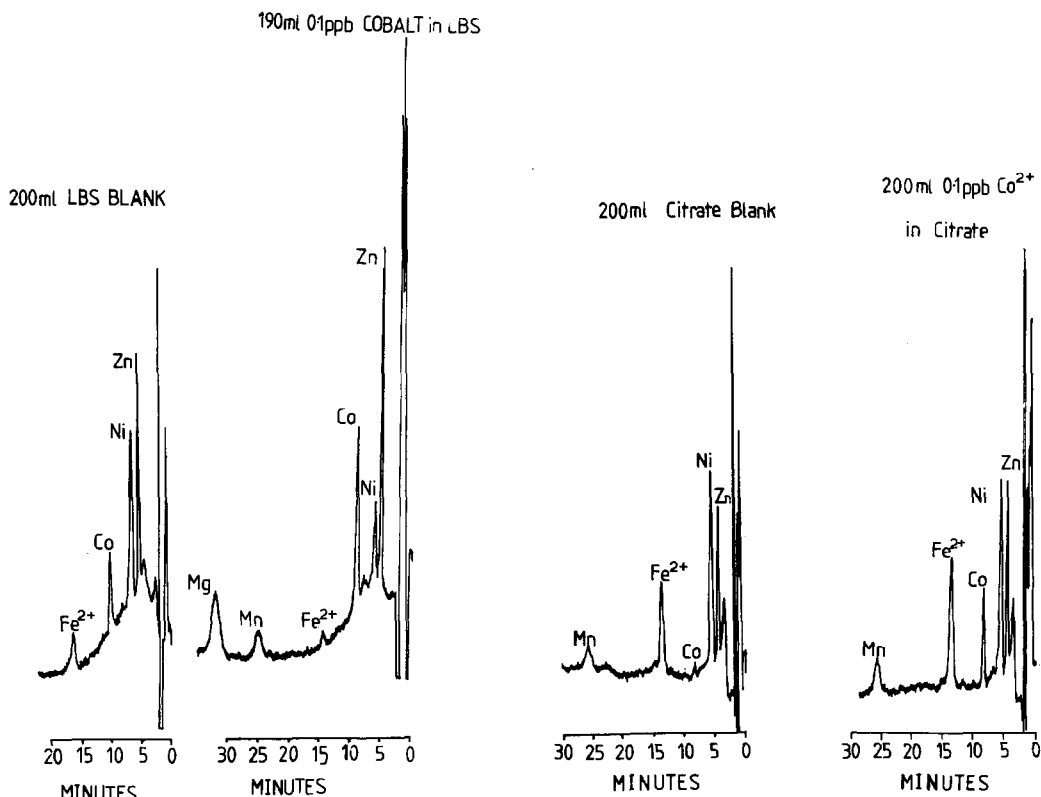


Fig. 4. Analysis of LBS, spiked with cobalt. Chromatographic conditions similar to Fig. 2.

Fig. 5. Analysis of citrate solution (0.001 M), spiked with cobalt. Chromatographic conditions similar to Fig. 2.

CONCLUSIONS

This work demonstrates the ability of HPLC systems to determine cobalt at pg ml^{-1} concentrations in the sample matrix of the primary coolant of a PWR. The performance of the preconcentration system gave quantitatively reproducible determinations with a good linear response over two orders of magnitude (2.5–100 ng). Blank levels could be reduced further and thus decrease the limit of detection, by additional purification of reagents using techniques such as recrystallization, manganese dioxide precipitation and constant electrolysis at a mercury pool electrode. The stability trials indicate the feasibility of the storage of samples for up to 7 days without adsorption losses when stabilized by a citrate buffer.

The system is easily automated and offers considerable flexibility with easily changed preconcentration and analytical columns, the precolumn also acting as a guard column. Sample volumes may be varied to suit requirements of either time or limit of detection, and the post-column reagents can be selected to vary both sensitivity and selectivity.

The system has been tried out on autoclaves at Winfrith Atomic Energy Establishment, and is presently being used for chemistry studies on a half Megawatt Loop, which simulates PWR operating conditions. Preliminary results have been very encouraging and have already shown the potential of the HPLC approach. The effect of varying PWR coolant chemistry on sub ppb cobalt levels could be monitored continuously where previously other methods had failed. Although not discussed here the detection of manganese, iron and nickel at the ppb level has also shown promising results and work is continuing on the multi-element performance of the developed HPLC system.

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