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Application and development of ion chromatography for the analysis of transition metal cations in the primary coolants of light water reactors

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ABSTRACT

This paper provides an overview of the application of ion chromatography for the analysis of nuclear power reactor coolants. It covers the development of sampling and on-line chromatography on operating plants in Europe for measuring soluble transition metals and, in particular, cobalt at part-per-trillion (ng/kg) levels. The results of the plant investigations are highlighted with respect to their importance in understanding factors influencing the minimisation of Occupational Radiation Exposure. Development of chemiluminescence as a post-column detection technique is also reported which has resulted in the ability to detect and measure one picogram of cobalt.

INTRODUCTION

An understanding of the behaviour of soluble transition metal ions, particularly cobalt, in the high-temperature coolant (310°C) of light water reactors is very important to identify the transport mechanisms, materials and chemistry issues responsible for the build-up of out-of-core radiation fields. Limiting such radiation fields results in lower radiation doses to operators (termed Occupational Radiation Exposure, ORE) during maintenance periods. Cobalt behaviour is particularly important, since naturally occurring cobalt-59 provides the source for its activated daughter product, cobalt-60. This radionuclide is a major contributor to out-of-core radiation fields in water-cooled power reactor plants. The transport and activation process in the primary system of a water reactor is shown in Fig. 1. The coolant provides the transport medium for corrosion and activation products both as soluble and particulate species.

Transition metal ion chromatography (IC) has been used to determine both soluble and insoluble elemental species in reactor coolants, and the use of γ-spectrometry on post-column separated fractions has permitted radiochemical information to be obtained. It has been necessary to give particular attention to the determination of soluble elemental

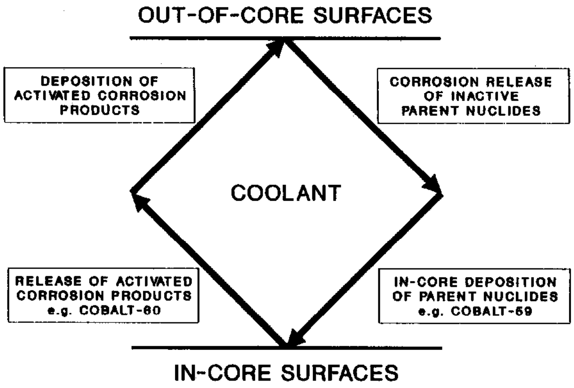

Fig. 1. Transport cycle for corrosion and activation products.

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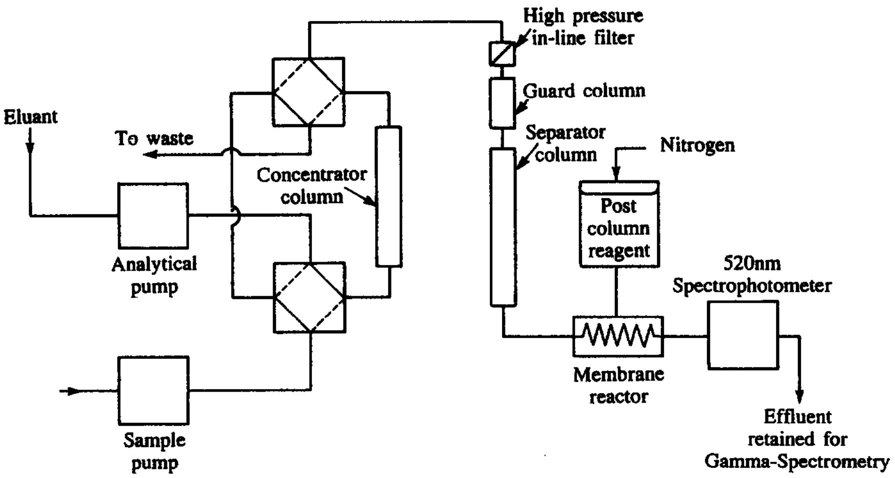

Fig. 2. Flow diagram for ion chromatography system.

cobalt at levels as low as 1 ng/kg (1 part-per-trillion). Soluble species have been determined directly following their on-line concentration from up to one litre of reactor coolant using spectrophotometric post-column detection. Much of the work reported here has been carried out using a Dionex 2003i series ion chromatograph coupled to a suitable microprocessor for data collection and processing (Fig. 2). Post-column detection based upon chemiluminescence has been pursued to elim-

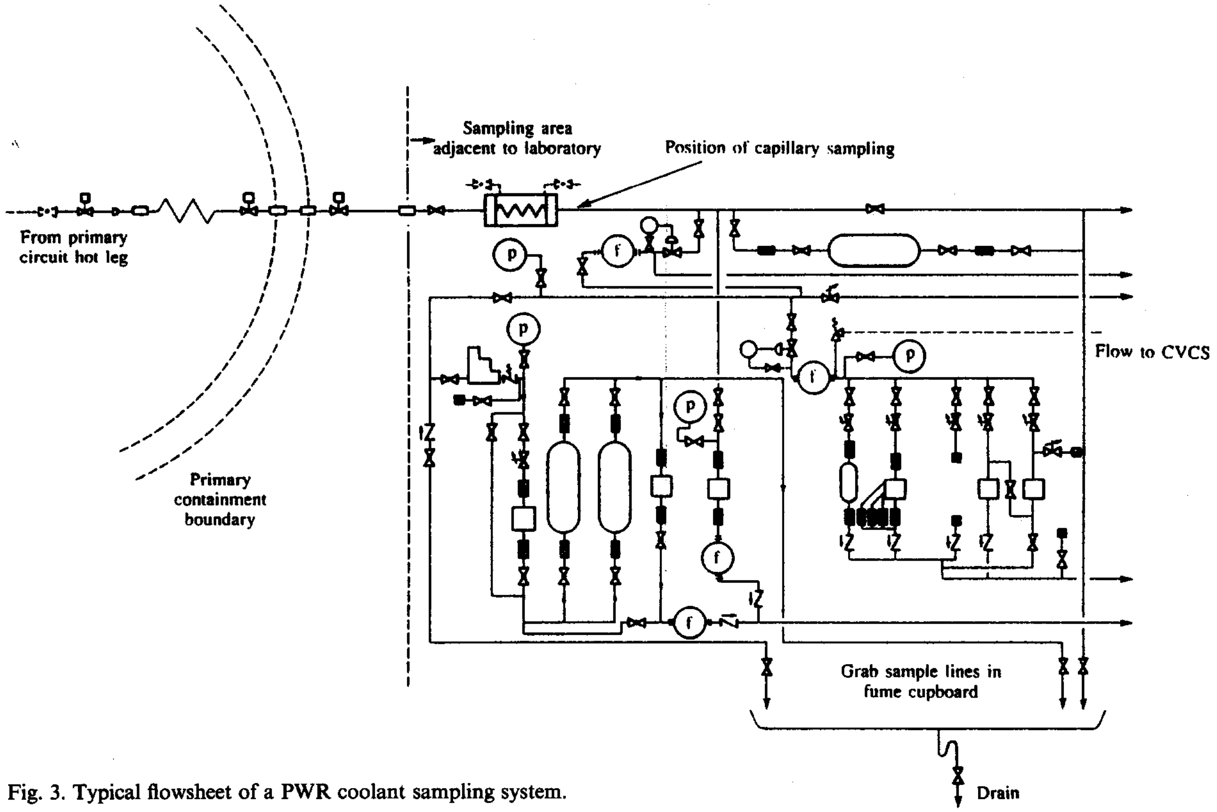

Fig. 3. Typical flowsheet of a PWR coolant sampling system.

inate the need for sample preconcentration. Insoluble species collected on filter membranes following filtration of up to 1500 l of coolant have been solubilised by potassium hydrogensulphate fusion prior to ion chromatography.

AEA Technology (UK Atomic Energy Authority) has collaborated for many years with a number of pressurised water reactor (PWR) utilities in Europe, and more recently with certain Eastern European water reactor utilities of the VVER design. Collaboration in fundamental chromatography research (*e.g.* chemiluminescence detection) has been undertaken with the University of Plymouth in the UK.

REACTOR SAMPLING

Conventional sampling systems for primary circuit coolant installed on commercial PWRs are essentially similar in design. Fig. 3 shows a typical flowsheet for a primary coolant sampling line at a Westinghouse plant. Routine grab sampling is carried out from a continuously flowing sampling line of 6 to 12 mm diameter by operation of relatively large valves. This can introduce pressure and flow perturbations in the system which can influence the measured values.

While generally satisfactory for the measurement of major soluble species required for reactor control, such as the boron and lithium concentrations, these basic systems have been shown to be unsatisfactory for both the representative sampling of particulate material and the continuous on-line determination of very low concentrations of soluble transition metal species such as cobalt and nickel. Capillary sampling has been employed to obtain better representation of particulate species and to provide unperturbed, continuous, low volume sam-

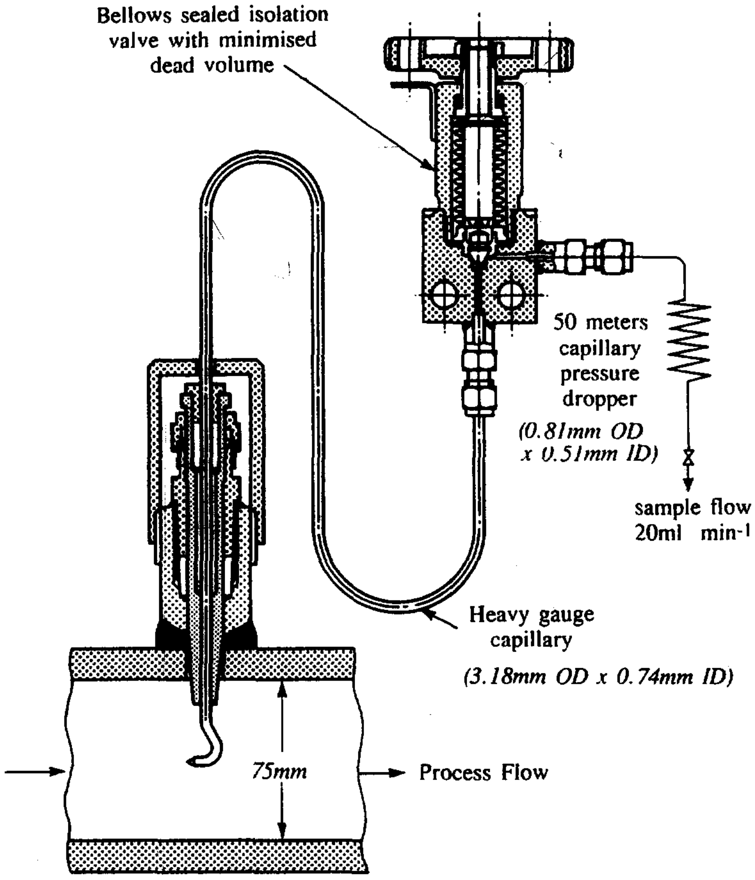

Fig. 4. Direct capillary installation in process line.

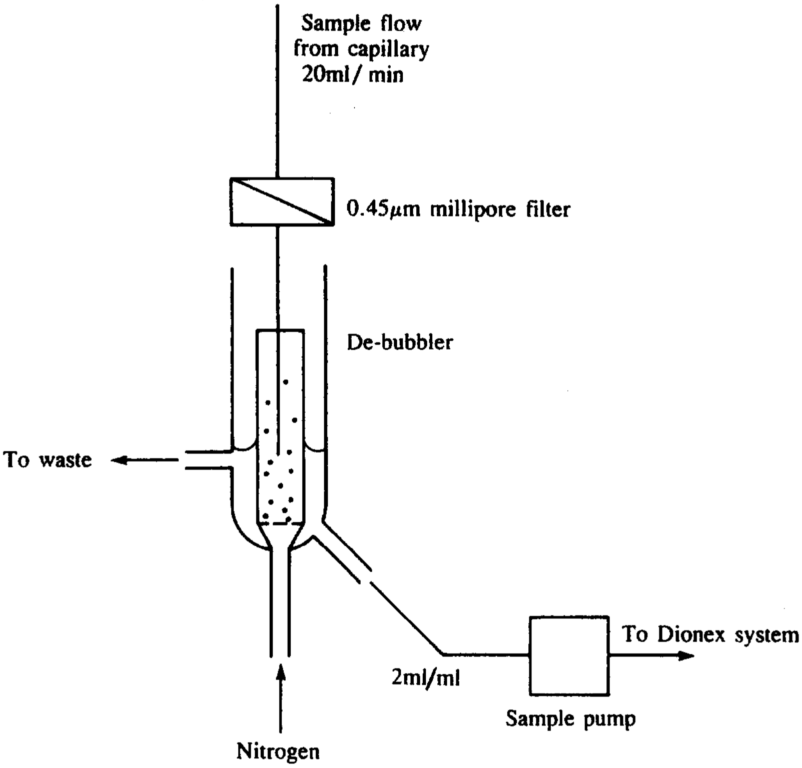

Fig. 5. Arrangement for hydrogen degassing of samples.

pling for the determination of soluble species. An example of a capillary sampling system installed on a high pressure (190 bar) reactor line is shown in Fig. 4. As far as possible, the fluid velocity in the capillary system is matched to that in the primary line from which the sample is being extracted in order to achieve iso-kinetic conditions.

Hydrogen, dissolved in the primary circuit coolant at pressure to prevent water radiolysis in the reactor core, is released in the form of very small bubbles following depressurisation within the sampling capillary. It is essential that these bubbles are removed before the sample is fed to the preconcentration pumping system of the ion chromatograph. The apparatus used on plant to achieve degassing of the coolant sample is shown in Fig. 5. Flow from the capillary passes through a 0.45-μm membrane filter to remove particulate matter. Hydrogen in the coolant is degassed using nitrogen and the coolant overflows into a constant head device which allows sampling by the IC pump.

Insoluble species, collected on the filter membranes after the passage of at least 200 l and up to 1500 l of reactor coolant, required some treatment prior to chromatographic analysis. The filter membranes were moistened with acetone and warmed gently in a silica flask to assist decomposition. The residues were fused with potassium hydrogensulphate until a clear melt was achieved. The "melts" were dissolved in ultra-pure water, and aliquots taken for IC analysis.

DEVELOPMENT OF CHROMATOGRAPHIC METHOD

A variety of methods for the separation and quantification of transition metal, lanthanide, and heavy metal ions have been reported based upon standard HPLC ion-exchange resins [1–3]. Cassidy and Elchuck [4] were able to modify reversed-phase material to act as a cation exchanger, a technique which allowed some control of the ionic capacity of the stationary phase. Organic acids, such as oxalic, citric and lactic, have been mainly used in transition metal ion separation, whilst spectrophotometry has been widely utilised for post-column detection. The use of mineral acids for the mobile phase can cause problems with transition metal analysis at ultra-trace levels, particularly if conventional steel HPLC systems are used. Indeed, at ultra-trace levels, even the use of organic acids can cause problems. Thus, either totally inert systems made from polymers or all-titanium systems are to be preferred for ultra-trace level work.

Jones *et al.* [5] demonstrated the separation and detection of cadmium, cobalt, copper, iron, lead, manganese, magnesium, nickel and zinc in about 45 min using an inverse photometric detector based upon Eriochrome Black T. This method was the first applied to the measurement of soluble transition metals in PWR primary circuit coolant [6]. Subsequently, Dionex transition metal IC has been extensively used in research studies into the behaviour of soluble transition metals in the primary circuit of a PWR both in out-of-pile research loops and operating power reactors and it has been adapted for on-line analysis [7,8]

Initially, cationic IC was employed for transition metal analysis, but this was changed to anionic separation with the development of improved ion-exchange material based upon anionic latex coating of surface sulphonated cation resins. Transition metal separation has been achieved by chromatography of metal–ligand anionic complexes. Organic chelating agents such as tartrate, citrate and oxalate form anionic complexes which are too stable for post-column derivatisation with spectrophotometric reagents such as 4-(2-pyridylazo)-resorcinol (PAR). Pyridine-2, 6-dicarboxylic acid (PDCA) forms stable complexes with all the transition metal ions of importance in primary circuit waters and allows their chromatographic separation. It also allows coloured complexes to be formed between the transition metal ions and the PAR used as the post-column reagent. Modifications to an original mobile phase reagent (6 m*M* PDCA adjusted to pH 4.8) were required to allow sequential analysis of the important trace elements. Determination of manganese required the addition of sodium sulphate and sodium chloride to the mobile phase.

Reliable quantification of the soluble iron content of coolant samples required a second modification to the PDCA-based reagent. Whilst technically possible to separate and quantify ferrous and ferric ions, in practice problems were experienced with erratic results due to changes in the oxidation state of iron during analysis. Reduction of all soluble iron species to the ferrous state was adopted for all reactor coolant analysis and this has allowed reliable and reproducible results to be obtained on the total soluble iron concentrations in the coolant. Additions of ascorbic acid, sodium sulphite and methanol were required to reduce any ferric to ferrous and prevent the development of damaging bacterial growths in the reagent. Such growths severely limit the shelf-life of the reagent to less than one day and could lead to deterioration in column performance and blockages.

The eluent and post-column reagents used in the reactor coolant studies were prepared as follows. For the eluant, 2.0 g of PDCA, 5.84 g of sodium chloride, 0.72 g lithium hydroxide monohydrate, 0.50 g of sodium sulphite and 0.57 g of sodium sulphate were dissolved in high purity water followed by the addition of 0.7 g ascorbic acid and 40 ml of methanol and the resultant solution diluted to 4 l with high purity water. The eluant was filtered through a 0.45-μm filter membrane. The post-column reagent was prepared by dissolving 0.1 g of PAR in 700 ml of deionized water followed by the addition of 180 ml of ammonium hydroxide solution (sp.gr. 0.880) and 67 ml of glacial acetic acid. This solution was diluted to 1 litre with further deionized water and filtered through a 0.45-μm membrane.

Pulse free addition of the post-column reagent was found to be particularly important for the trace level measurement to ensure minimum baseline noise. This was achieved using a Dionex membrane reactor where the PAR reagent diffuses under nitrogen gas pressure into the column eluent through a permeable fibre membrane.

Elution of the transition metal ions was typically achieved in 20 min and a representative chromatogram from a reactor coolant sample is shown in Fig. 6A with peak data shown in Table I. The same chromatogram is shown in Fig. 6B with five times expansion and baseline correction. Limits of detection, based upon 4.65 standard deviations of the background/blank noise, were 1 ng for nickel and 0.5 ng cobalt. In practice, the limit of detection is influenced by the resolution from and the magnitude of the peaks eluting before and after the element of interest. The maximum volume of coolant which was practical to preconcentrate was one litre which gave a limit of detection of 0.5 ng/kg cobalt (or 0.5 ppt).

REACTOR MEASUREMENTS

Using the sampling and analytical techniques described, measurements of soluble transition metals, and in some cases insoluble and radiochemical species, have been made on a number of European PWRs [9]. Analytical measurement campaigns for transition metal ions have been made on five Westinghouse designed plants, four Kraftwerk Union (KWU) and four Soviet designed VVER-440. Measurements have been made during steady full power operation close to mid-cycle, and at some reactor start-ups and shutdowns. Table II summarises the results of a number of the measurements made during steady operation at mid-cycle for each plant. As far as possible the plants are arranged in descending order of soluble elemental cobalt concentration measured in the primary coolant whilst retaining the plant groupings.

Both the Westinghouse plants and the earlier KWU plant (C) have high cobalt alloys (Stellites) within the primary coolant circuit, including significant in-core components and, apart from plant B, show the highest concentrations of soluble elemental cobalt. In the later KWU stations, represented by plants D, E and F, a policy of progressive replacement of Stellites and control of cobalt in structural materials has been pursued, and the benefits of this are clearly reflected in the soluble concentrations of cobalt in the coolant. Plant G, the Soviet designed VVER-440 unit, gave the lowest soluble elemental cobalt values of any plant monitored. Such measurements have been confirmed in further analyses carried out at two additional VVER-440 units in Eastern Europe. High cobalt containing

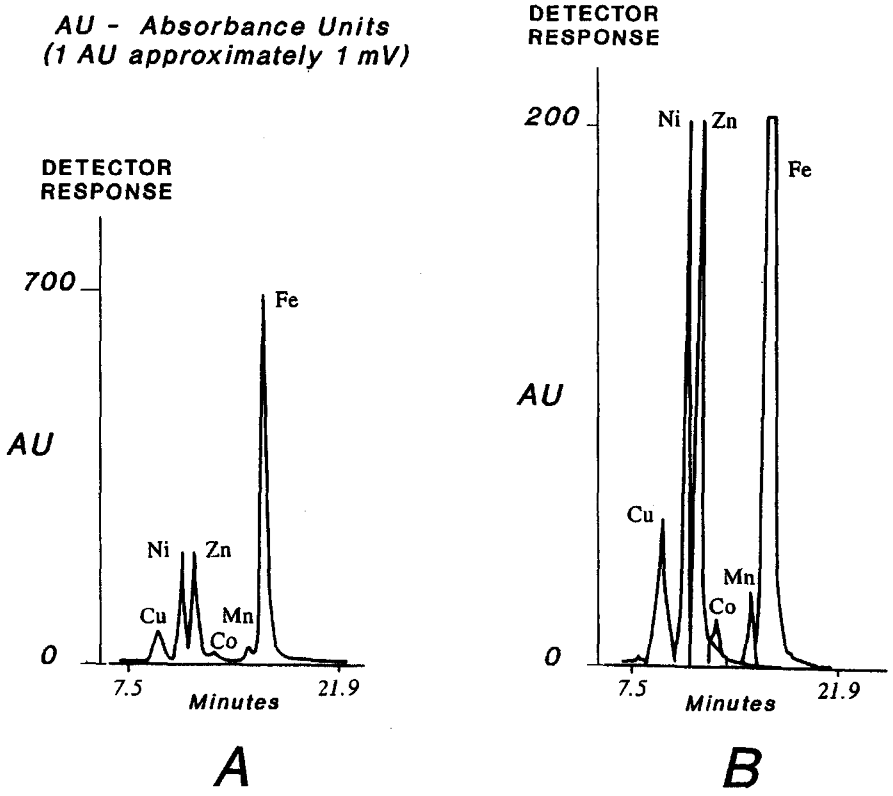

Fig. 6. Typical chromatogram from a PWR primary coolant.

TABLE I

PEAK DATA FOR TYPICAL PWR COOLANT CHROMATOGRAM SHOWN IN FIG. 6

Element	Loading (ng)	Retention time (min)	Peak height	Peak area
Cu	22.5	8.50	55	1059
Ni	90	9.40	211	4499
Zn	180	10.27	210	5329
Co	4.5	11.47	10.9	253
Mn	18	13.73	27	815
Fe	675	14.70	760	29 982

Stellite alloys have not been used in the VVER design of plants and other differences from Westinghouse and KWU plants can be found in the primary circuit chemistry and heat exchanger surfaces. Heat exchanger surfaces are stainless steel in VVERs compared with nickel-based alloys in Westinghouse and KWU plants, also the primary circuit chemistry operates with ammonia–potassium hydroxide–boric acid as opposed to a lithium hydroxide–boric acid regime. The relationship between measured levels of soluble elemental cobalt circulating in the primary circuit coolant and the observed out-of-core radiation dose rate (as measured at the channel head of the steam generator) appears to be independent of reactor type (Fig. 7). The most important factor would appear to be the cobalt inventory of the circuit, an indication of which is provided by the transition metal IC measurement.

POST-COLUMN DETECTION BY CHEMILUMINESCENCE

Greater sensitivity for cobalt determination was desirable for the unambiguous resolution of the cobalt peak from the chromatographic background, as a confirmatory detection system for cobalt peak identification, and to avoid long preconcentration times associated with collecting one litre of reactor primary coolant. Whilst alternative spectrophotometric reagents might be identified which had greater selectivity and/or sensitivity for cobalt, it was unlikely that any reagent would have the necessary "orders of magnitude" increase in its molar extinction coefficient compared with PAR. A different approach was considered necessary for any significant increase in sensitivity, since, within a small factor, the ultimate potential of molecular absorption would appear to have been reached.

Luminescence methods were thought to offer considerable scope for development and of all the

TABLE II

PRIMARY CIRCUIT COOLANT MEASUREMENTS ON EUROPEAN PWRs

Plant	Boron (mg/kg)	pH 300°C	Elemental Co (ng/kg)		Co-60 (Bq/kg)		Specific activity (GBq/g)		Elemental Ni ng/kg)	
			Sol.	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.	Insol.
(A) Westinghouse (Cycle 3)	840	7.23	10.0	–	430	–	43	–	280	–
(B) Westinghouse (Cycle 13)	489	7.00	4.0	0.52	78	50	20	96	334	135
(C) KWU (Cycle 13)	450	7.29	9.0	–	730	–	81	–	87	–
(D) KWU (Cycle 4)	380	7.35	7.9	–	1670	–	211	–	39	–
(E) KWU (Cycle 4)	300	7.42	2.0	0.19	180	24	90	126	32	58
(F) KWU (Cycle 1)	440	7.30	1.8	0.20	59	5	33	25	21	26
(G) VVER 440 (Cycle 13)	594	7.32	1.1	0.14	6	1.14	5.5	8.1	83	13

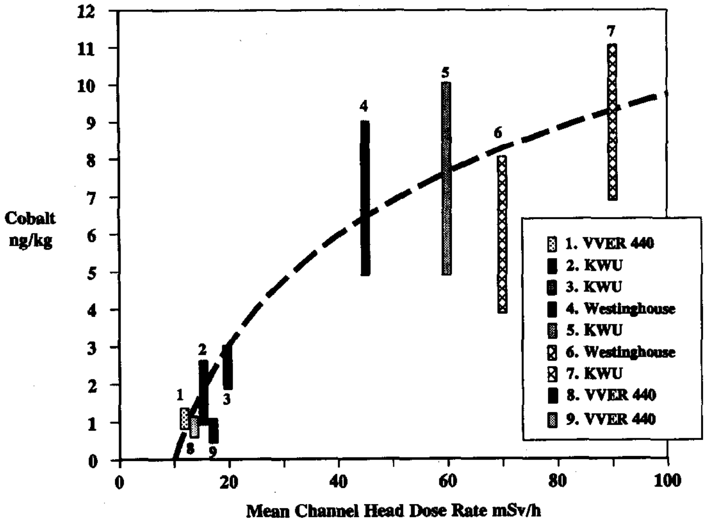

Fig. 7. Comparison of soluble elemental cobalt in the primary coolant with channel head dose rate.

techniques, chemiluminescence was considered to be the most suitable for ultra-trace cobalt analysis. The earliest reported use of chemiluminescence for the analysis of transition metal ion was for cobalt by Babko and Lukovskaya in 1963 [10]. Despite the limitations of photographic plate detection, an absolute detection limit of 2 ng cobalt was obtained. Development of flowcell systems in the early 1970s led to a method for the separation and quantification of cobalt and copper based upon HPLC and chemiluminescence [11]. However, high-efficiency ion-exchange materials were not available at that time, so the chromatographic separation was relatively poor.

Boyle *et al.* [12] used a luminol post-column reaction system with HPLC to determine cobalt, but this method required elaborate sample handling and a multiple-valve chromatographic system. More recently the technique has been used to measure cobalt in seawater at trace levels using a relatively simple flow injection system [13]. Whilst the absolute amount of cobalt detected in this case was only comparable with the existing HPIC–spectrophotometric detection (0.5 ng cobalt), further potential of the detection system was considered possible. Preliminary studies undertaken at the University of Plymouth (previously Plymouth Polytechnic) indicated that very high sensitivity could be achieved using luminol–hydrogen peroxide chemiluminescence.

Luminol chemiluminescence

Certain metal ions catalyse the reaction between luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) and hydrogen peroxide. In excess of the reagents, the degree of chemiluminescence observed is directly proportional to the metal ion concentration over several orders of magnitude [14]. Catalysis of the luminol reaction is inherently non-selective, but certain metal ions have a greater effect than others. Cobalt is second only to chromium in its sensitivity as a result of its ability to catalyse the luminol–peroxide reaction.

Catalysis of the chemiluminescence reaction by cobalt would be affected by other competing reactions such as the strength of the cobalt-eluent ligand bonds. Thus, application of chemiluminescence as a post-column detection technique for HPIC required changes to the chromatographic separation conditions and eluent used to prevent interference.

Chemiluminescence detector

Detectors for chemiluminescence detection can be characterised by their simplicity. A suitable detector was constructed in a light proof housing (Fig. 8) which contained a photoreceptor. Cables and re-

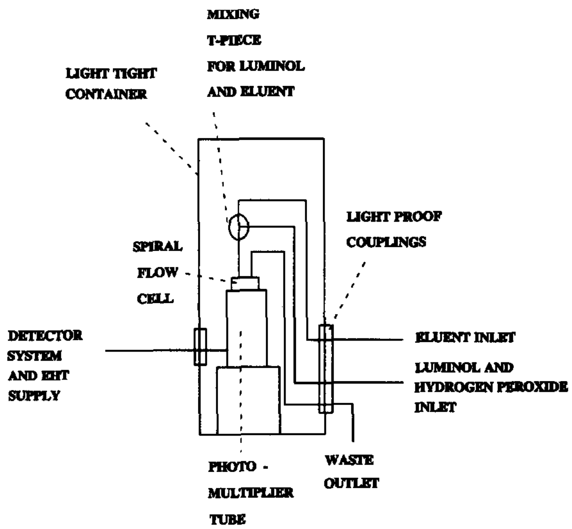

Fig. 8. Chemiluminescence detector.

agent lines passed through light-proof couplings into the container to minimise the amount of adventitious light reaching the photoreceptor. The photoreceptor used was a flat-faced photomultiplier tube (Thorn EMI type 6097) having a spectral range of 330–680 nm, and a maximum sensitivity at 450 nm.

An optical coil flowcell was constructed from narrow bore transparent PTFE tubing as a 45-mm diameter flat spiral. The coil was wound from the centre outwards, returning again to the centre. This shape of coil flowcell maximised the area/volume of the eluent in contact with the detector. The total volume of the flowcell was 200 μl, giving a residence time of about 5 seconds. A matt black backing disc was mounted behind the flowcell to reduce any stray incident light.

Chromatographic conditions for chemiluminescence detection

Spectrophotometric detection utilised in the measurements made on power stations relied upon the anionic separation of transition metal–PDCA complexes. However, it was necessary to revert to the use of cation-exchange material for chemiluminescence post-column detection because of effects of ligand complexation. PDCA complexes were considered to be too stable to permit release of cobalt ions to catalyse the luminol–peroxide reaction.

Early attempts at cobalt determination using high-capacity cation-exchange material with a tartrate-based eluent gave poor results in terms of sensitivity [15]. Strong suppression of the chemiluminescence response was observed as a result of the presence of tartrate. Low capacity ion-exchange material was required with the use of an eluent with a lower chelating ability than tartrate. Dionex cation ion-exchanger C2, having high efficiency and low ion-exchange capacity, had already been shown to give good separation of transition metals in reactor plant applications with a lactate-based eluent and spectrophotometric detection [7].

A suitable HPIC system was established with a chemiluminescence detector and most of the work carried out using a 5-cm long Dionex C2 resin column. Optimum pH for the 0.12 *M* lactic acid eluent was found to be 3.8 with ammonium hydroxide being used for pH adjustment [16]. Elution order determined by spectrophotometric detection was iron(III), copper, zinc, nickel, cobalt, iron(II), and manganese. At a lactate eluent flow-rate of 1.2 ml/min, cobalt was eluted after approximately 13 min.

Following optimization of the chromatography conditions, attention turned to optimization of the chemiluminescence detection. Copper was found to give a large response, but the response was strongly dependent upon the alkalinity of the luminol–peroxide reagent [16]. Post-column reagent conditions were selected such that the resultant pH of the combined column eluent–luminol–peroxide solution was greater than pH 10. The post-column reagent was prepared by dissolving 0.1 g luminol and 3 g boric acid in 500 ml of ultra-pure water containing 5 ml of hydrogen peroxide. This solution was adjusted to pH 12 using potassium hydroxide.

A typical response trace of the chemiluminescence determination of cobalt in a PWR coolant sample is shown in Fig. 9 which can be compared with spectrophotometric detection shown in Fig. 6B. The specificity of the method is demonstrated by the absence of other peaks in the chromatogram (Fig. 9) and the stability of the baseline is particularly notable. Sensitivity of the detection systems was found to be good with more than a thousand-fold increase when compared with spectrophotometric detection. The limit of detection was found to be 0.3 pg cobalt compared with 0.5 ng cobalt for spectrophotometric detection.

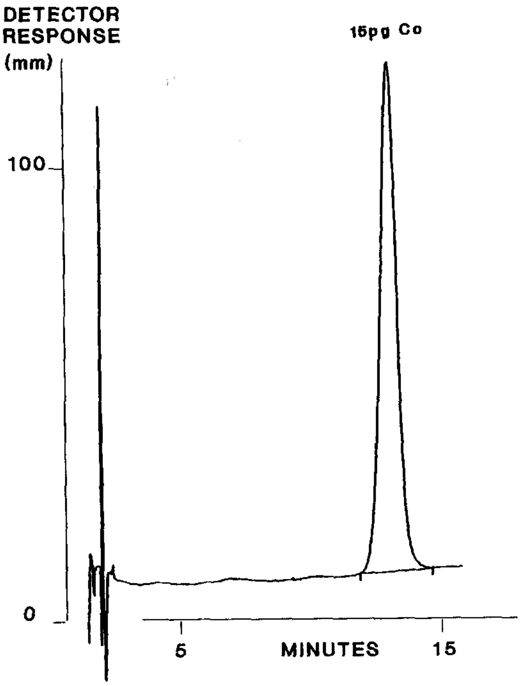

Fig. 9. Chemiluminescence detection of cobalt in PWR coolant samples.

COMPARISON OF DETECTION TECHNIQUES

One inherent weakness in all chromatographic analysis is the unambiguous identification of peaks, but the use of more than one detection system is able to resolve such uncertainties. Conclusive evidence of the validity of the cobalt determinations on PWR primary circuit coolants by the spectrophotometric detection technique was achieved by the application of chemiluminescence detection.

There was a marked contrast in the sensitivity and clarity of the specific chemiluminescent determination of cobalt and the standard multi-element technique based upon anion-exchange and spectrophotometric detection. A peak of only 15 pg cobalt measured by chemiluminescence detection (Fig. 9) can be compared with the peak produced by 4500 pg cobalt using the PAR spectrophotometric approach (Fig. 6B).

Typically, the maximum volume for direct injection in chromatographic procedures is 500 μl, and this enables cobalt concentrations in PWR coolants to be measured when present at *ca.* 0.5 ng/kg (0.5 ppt) using chemiluminescence detection. Spectrophotometric detection requires the preconcentration of one litre of coolant for such ultra-trace levels. Thus, more convincing results are likely to be obtained from the former technique when cobalt concentration are at or below the 1 ng/kg level. However, such sensitivity may only be required for specific applications or investigations, and at other times a multi-element capability will be more important that high sensitivity/specificity.

CONCLUSIONS

Ion chromatography has been successfully demonstrated and used for the on-line determination of soluble transition metals in PWR primary coolant, with a detection limit of less than 1 ng/kg achieved for cobalt.

Determination of cobalt in the primary coolant of PWRs has led to observations concerning important factors influencing the build-up of out-of-core radiation fields. In particular, the relationship between soluble cobalt levels in the coolant of a water-cooled power reactor and the out-of-core radiation field appears to follow a trend irrespective of reactor type. There is evidence of a correlation between the soluble cobalt levels in reactor coolant with the progressive removal of high cobalt containing alloys and the control of cobalt levels in structural materials of the primary circuit. Data obtained by ion chromatography measurements remain a diagnostic tool with respect to systems materials effects.

Capillary modifications to existing sampling systems have proved an excellent means of providing a continuous, representative, low volume sample flow to analytical instrumentation, eliminating problems associated with the perturbations caused by grab sampling.

Chemiluminescence has been shown to have potential as a highly specific and sensitive post-column detection system for the ion chromatographic determination of cobalt. Absolute detection of 0.3 pg cobalt has been achieved which allows direct injection of samples of PWR coolant when the cobalt concentration is only at the 1 ng/kg (1 part-per-trillion) level.

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