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TRACE METAL DETERMINATION BY CHROMATOGRAPHY

G. NICKLESS

School of Chemistry, University of Bristol, Bristol (U.K.)

CONTENTS

1. INTRODUCTION

It is the reviewer's brief to assess the current status, to discuss the recent advances and developments within the chosen area and if possible to look to the future of the topic.

Undoubtedly the most versatile systems in the recent past for the separation and determination of species present in chemical mixtures have involved the use of chromatography. The analytical procedure for the separation of complex organic compounds which does not employ chromatography is more the exception than the rule. However, chromatography is a means of separation and is not a determinative procedure. Thus when quantitation is required, the combination of a chromatographic procedure coupled or united to a technique of determination has to be implemented[1]. This particular aspect of the system was realised almost at the birth of inorganic chromatography and the work of Lacourt and co-workers[2,3], Lederer and co-workers[4–8], Pollard and McOmie[9] and Wells and co-workers[10–12] bear testimony to their vision. So "hyphenated" methods are not new.

The appropriate forms of chromatography dependent upon the chemical and physical characteristics of the species to be separated have had to be developed[13]. Because of the ease of volatility of most organic compounds, gas–liquid chromatography has been and still remains a major force in organic separations and analysis although more recently even its predominant position has and is being challenged by modern liquid chromatography[14]. However, at all times molecular identity is of paramount importance and interest.

On the other hand, the determination of inorganic compounds, particularly metals, has in the past amounted to little more than an elemental analysis. The normal techniques for this task have in the majority been spectroscopic methods, especially destructive ones where absorption photometry and then molecular spectro-

photometry were first dominant but were overtaken by emission techniques such as arc or spark optical spectroscopy or non-destructive X-ray fluorescence methods In turn, these, particularly emission, techniques yielded to atomic absorption procedures initially using flames as excitation sources were soon followed by electrothermal techniques Even these techniques are not completely secure because they are threatened by inductively plasma emission systems or inductively coupled plasma mass spectroscopy where the ability to determine the isotopic distribution of metallic elements is now available For the Plasma Quad, multi-element analysis with detection limits of a few tens of parts per trillion (10^{-12}) can be obtained, isotopic ratios can be directly measured with a high level of automation and precision[15,16]

Within the past decade, especially in the field of toxicology and the cycling of metals in the environment, the term "speciation" has become increasingly important Spectroscopic methods usually cannot by themselves yield the distribution or format of species of a particular element and so electrochemical procedures, particularly anodic stripping voltammetry, has been of much interest being used with great succes by Florence and Batley[17-19]

But even here the use of a separation medium which causes minimum disturbance to the system, namely a chelating ion-exchange resin (usually Chelex-100) is crucial to the success of the analytical scheme But even here the role of that surface is often not appreciated[20]

Most metallic compounds or moieties as a direct result of their ionic nature (in the solid or liquid phases) cannot be directly volatilized at the temperatures used in commercially available gas chromatographs Therefore, early studies of the chromatographic behaviour of metal ions centred around liquid-phase techniques such as adsorption, partition or ion-exchange modes either in column[21] or planar[22] forms Classical liquid column and paper chromatography are now far less widespread in their use than thin-layer chromatography in inorganic analysis and most of the work using these techniques dates from before the 1970's Although much initial success in the separation and quantitative determination was achieved, the techniques were extremely time-consuming and tedious, so the column and paper techniques soon fell into disuse Ion-exchange procedures were primarily used for the enrichment of trace elements from large volumes of aqueous solutions, preliminary fractionations or occasionally separation sequences[23] Such techniques yielded aqueous effluents which could easily be incorporated into suitably modified determinative photometric or electroanalytical procedures and so continued to receive attention[24-26] On the other hand, the inefficiency of partition column chromatography and the problems of complete elution or recovery of solutes from planar systems forced the development of more versatile methods of determination such as densitometry after planar separation[27-29] However, as direct comparison (between different paper or thin-layer chromatographic techniques) of the quality of quantitative results achieved is frequently not possible, individual research workers offer widely differing information for the characterisation of the method employed Non-uniformity of detection limit, determination range or deviation from the true amount were more the rule than the exception Therefore, it is little wonder that quantitative inorganic chromatography using the liquid phase can be termed to have only "hung-on" during the halcyon days of atomic absorption spectrometry

2 GAS CHROMATOGRAPHY

With the rapid growth in gas chromatography, research workers were not slow to try to exploit the technique and simple volatile inorganic gases, halides and hydrides were separated, mainly by gas–solid adsorption techniques[30,31] However, for metal ions, the problem of volatility still remained It is now nearly thirty years since Lederer[32] suggested that the formation or use of neutral metal chelate complexes such as acetylacetonates might be suitable for elution through a gas chromatographic column Thus although inorganic gas chromatography is a firmly established technique, some twelve years ago, all Russel and Tolg[33] could quote were 600 publications apertaining to the "Application of gas chromatography for the separation and determination of inorganic substances" and a similar number were reported by Guiochon and Pommier[34] Only about 10% of the references were concerned with the studies of metal complexes and possible application of such studies, showing quite clearly that the field has grown very slowly particularly in the development of acceptable procedures for metal determinations via derivatization/complexation procedures following the pioneering work of Moshier and Sievers[35]

Because of the large number of articles and documents available on this field, the reviewer will be strained to say anything which is original, but is the intention to try to discuss the current status of chromatography for metal determinations in terms of the phases used for the separation namely

(a) gas phases

(b) liquid phase (i) planar modes

(ii) column modes

Because of Professor Uden's lecture comments upon gas-phase separations will be very severely curtailed Uden and Henderson[13] list some eight constraints or factors that have to be overcome to allow further procedural development for the determination of metals by gas chromatography For sake of completeness they are reiterated here

(1) Type of complex restricted to neutral highly stable species, limiting choice effectively to chelate structures

(2) Unhelpful column interactions, especially at the submicrogram level of concentration

(3) The realisation (albeit slowly) that ligand systems other than β-diketones were potentially useful

(4) Most useful ligands were often unavailable except by synthesis by the research worker concerned

(5) A distinct lack of quantitative chelation reactions in the liquid (or vapour phase) which are absolutely essential for valid analytical method development In addition there has been a lack of development of the necessary analytical quality control strategems describing the procedures to be adopted

(6) The over-riding need to devise reaction/extraction procedures that were better or more competitive than those used in non-separating procedures such as spectroscopy, etc

(7) The risk involved in (not being successful) or need to exploit novel chromatographic conditions or requirements to overcome the irreproducibility of analysis

(8) Prejudice in the minds in the non-chromatographers especially spectroscopists who have spent a great deal of time and effort exploring their own techniques without recourse to the concepts of chromatography

The two developments which appear to have taken place since the Uden and Henderson review[13] are the gradual replacement of the conventional packed column by fused-silica capillary columns and the elimination of the conventional gas chromatography detectors such as flame ionisation and even electron-capture detector by more selective detection processes based on atomic absorption spectrophotometry[36,37], microwave induced emission[38,39] or inductively coupled plasma modified flame photometric detection[40-42] systems, thus achieving greater selectivity and comparable sensitivity and so obviating any need for "clean-up" procedures prior to gas chromatography The ultimate detector, the mass spectrometer, has achieved only limited use for the determination of inorganic substances following gas chromatography But extremely high sensitivity, $e g$, 10^{-14} g (0 01 pg) for the fluorinated lead diketonates has been reported[43] With packed columns the selectivity of the mass spectrometer is lower than that of the flame photometric, or atomic absorption systems[44 45]

At the present time, there is much interest in transformation reactions of metals and metalloids as they pass through the environment or through mammalian systems where speciation is of prime importance For example, there is interest in the excretion of methyl arsenicals from selected human subjects[46] Indeed the production of trimethyl arsine has been reported[47] The species involved include inorganic arsenic, monomethyl arsonic acid, dimethyl arsonic acid In 1975 a gas–liquid chromatographic separation of these species was reported[48] after preparation of the respective diethyldithiocarbamates The separation was applied to the determination of inorganic and methylated arsenicals in urine and water Separation involved a suitably silanized 5% (w/w) OV-17 on Anakron AS as packing and electron-capture detection Recovery data were obtained which were satisfactory [inorganic As (1 0 μ/ml), 82 6 $\pm$ 7 7%, monomethyl (0 5 μg/ml), 91 5 $\pm$ 7 0%, dimethyl (0 5 μg/ml, 100 $\pm$ 4 0]

Two similar procedures were reported in 1983, where the determination of arsenite, arsenate and monomethyl arsonic acid in aqueous samples by gas chromatography of the 2,3-dimercaptopropranol (BAL) complexes was reported[49] The arsenicals (after selective reduction or ppt ion reactions to the trivalent state) were complexed with BAL, extracted and injected into the gas–liquid chromatograph, flame photometric detection at 384 nm was used Good recoveries (92–103%) and low detection limits of the order of 0 02 ng for arsenate and arsenite were reported Gas chromatography and multiple ion detection mass spectrometry after a hydride generation–n-heptane cold trap system was described by Odanaka et al[50] for the quantitative determination of inorganic arsenic, monomethyl, dimethyl and trimethyl arsenic compounds Arsine and methyl arsines produced by sodium borohydride reduction were first collected in a heptane ($-80°C$) cold trap and then subjected to gas–liquid chromatography The detection limit for a 50-ml aqueous sample was between 0 2 and 0 4 ng/ml of arsenic for such arsenic compounds Relative standard deviations ranged from 2% to 5% for distilled water replicates spiked at the 10 ppb (10^9) level Recoveries of all four arsenic species from soil and plant extracts, urine or river water ranged from 85 to 100% Trimethyl arsenic compounds were detected as a new metabolite in the urine of laboratory animals involved in an investigation

of the biomethylation of arsenic compounds following ingestion

Several recent papers have described various aspects of the determination of alkyllead species using gas chromatography after alkylation with a suitable Grignard reagent Thus an analytical procedure was described for the determination of trialkyllead compounds in aqueous media[51] The analyte compounds were extracted into benzene from an aqueous solution saturated with sodium chloride They were quantitatively converted into the respective n-butyl trialkyllead compound Precolumn Tenax trap enrichment of the derived tetraalkyllead enabled determinations into the low-ppb region Separation was achieved using an SP-2100-coated fused-silica capillary column (12 5 m $\times$ 300 μm O D $\times$ 200 μm I D) Specific lead detection was determined by atmospheric pressure microwave induced plasma emission Data were attained for the analysis of a waste water effluent sample which contained some 600 ppb total lead (determined by direct current plasma–optical emission spectroscopy) and 19 0 $\pm$ 4 0 ppb of triethyllead [$(C_2H_5)_3 Pb^+$] Trimethyllead [$(CH_3)_3 Pb^+$] was less than 5 ppb and further concentration steps had to be used

Thus work could now proceed on a studies of the environmental fate and toxicity of organolead complexes because the determination of dialkyllead and trialkyllead, (R_2Pb^+ and R_3Pb^+ where R = CH_3 or C_2H_5) is of paramount importance in understanding their metabolic pathways and toxicity It has been shown that inhalation or absorption of tetraalkyllead compounds resulted in the formation of R_3Pb^+ in the fluids and tissues of rats[52], human[53] and fish[54] Chau et al[55] have elegantly exploited the butylation process, firstly developing a procedure for the determination of dialkyllead, trialkyllead, tetralkyllead and lead(II) ions in water by extraction into benzene following chelation with diethyldithiocarbamate The lead species were butylated to the respective tetraalkyllead form, $R_nPb(C_4H_9)_{4-n}$, R = CH_3 or C_2H_5, all of which could be separated and quantified by gas–liquid chromatography–atomic absorption spectrometry A detection limit of 0 1 μg l^{-1} of lead was achieved using a 1-l sample Other metals co-extracted by the chelating agent do not interfere In a very recent publication[56] the scheme has been amplified to include ten organolead species in sediments and biological samples Some five tetraalkyllead species ($R_n'R_{4-n}''$ Pb, R$'$ = CH_3, R$''$ = C_2H_5), four dialkyl- and trialkyllead (R_2Pb^+ or R_3Pb^{2+}, R = CH_3 or C_2H_5) and ionic lead (Pb^{2+}) were determined (Table I) The data supporting the analytical quality control achieved are detailed and in general satisfactory although low recoveries of $(CH_3)_2Pb^{2+}$ from fish are to be noted Samples of fish and macrophytes (weeds) from the St Lawrence River at Maitland, Ontario, Canada, are quoted, indicating the method is viable on real samples

An important feature of the method is the simultaneous separation and determination of dialkyl-, trialkyl- and tetraalkyllead compounds as well as inorganic lead(II) in their authentic forms without calculations based on difference For the first time the occurrence of triethyl- and diethyllead compounds was confirmed in fish samples Unknown peaks were found, from the values of their retention times it could be postulated that they are dialkyl- or trialkyllead compounds with mixed alkyl groupings, e g $(CH_3)(C_2H_5)Pb^{2+}$ No doubt further investigations using this concept will take place in the near future with judicious choice of sampling sites

Not surprisingly a similar chain of events is beginning to emerge concerning the determination of butylated tin(IV) species[57] which find widespread use as anti-

TABLE 1

LEVELS OF ORGANOLEAD COMPOUNDS IN BIOLOGICAL TISSUE AND SEDIMENTS[56]

All values are on a wet-weight basis, in ng/g

Sample	Concentration (ng/g)									
	$(CH_3)_4Pb$	$(CH_3)_3Pb^+$	$(CH_3)_2Pb^{2+}$	$(CH_3)_3-C_2H_5Pb$	$(CH_3)_2-(C_2H_5)_2Pb$	$CH_3-(C_2H_5)_3Pb$	$(C_2H_5)_4Pb$	$(C_2H_5)_2Pb^{2+}$	$(C_2H_5)_3Pb^+$	Pb^{2+}
Carp	137	2735	362				780	707	906	1282
Sediment				142	1501	3613	1152	22	187	10,000
Macrophytes (mixed weeds), 4 m deep				38			16,515	113	558	59,282

fouling points, stabilizers for poly(vinyl chloride), etc The alkyl derivative used in this case is the pentyl group which is attached to the dibutyl- or tributyltin species by the usual Grignard reaction The rection was originally developed for determination of butyltin species in water[58,59] and has now been modified to use atomic absorption as the detection sytem rather than a flame photometric detector[60] Although flame photometry using a filterless system and heated quartz tube atomic absorption detection systems have been investigated and are of comparable sensitivity, atomic absorption spectrometry with its potential applicability to other volatile organometallic compounds is now preferred[60] The "pentylation" reaction has now been applied to the levels of butyltin and inorganic tin species in harbour sediments[61] The most toxic of the butyltin species, tributyltin, was present at 0 5 mg/kg (dry weight) in the top 2 cm of Toronto Harbour In addition methyltin and dibutyldimethyltin were also found in the sediments of a few harbours investigated, indicating that the butyl tinspecies can be methylated in the aquatic environment As the ethyl- and methyltin species are more toxic than the higher alkyl group tin species used commercially, tin methylation would represent an increase in the toxicity of tin compounds Rather surprisingly biomethylation possibilities for R_2Sn^{2+} and R_3Sn^+ species appear not yet to have been investigated either *in vitro* or in aqueous sediment systems Methylation of lower tin species to (say) the trimethyl stage might also be important Generally, $R_3Sn^+ > R_2Sn^{2+} > RSn^{3+}$ in terms of toxicity Tin methylation is by no means an academic question only, in 1975 more than 25,000 tons of organotin compounds were manufactured worldwide[62] Another separation of mono-, di- and trimethyltin chlorides from tetramethyltin has recently been reported[63]

The other alkylmetal species of interest, namely methyl- and ethylmercury have received little attention since the early flurry of activity[64] but recently James[65] has used gas–liquid chromatography as a screening procedure for methylmercury in tuna and sword fish The gas–liquid chromatographic method compares favourably with the official AOAL atomic absorption method[65] The determination of dimethylmercury using gas–liquid chromatography and mass spectrometry has also been reported recently[66] A detailed paper reporting the determination of alkylmercury compounds in sea water using gas–liquid chromatography and atmospheric pressure helium microwave induced plasma emission spectrometry has been published[67] The detection limits for CH_3HgCl, C_2H_5HgCl and $(CH_3)_2Hg$ were 0 09, 0 12 and 0 40 $\mu g/l$, respectively, using peak height analysis with a dynamic linear range of more than four orders of magnitude For the levels of alkylmercury compounds in sea water, even these levels were insufficiently sensitive and a preconcentration step using cysteine/benzene had to be employed

Turning from methylated species to metals, the determination of beryllium at extremely low levels using the gas–liquid chromatographic behaviour of the trifluoracetylacetonate has been known for some considerable time and has been widely exploited[68] The method usually requires a two-phase, two-component solvent system, involving long reaction times and high temperature of reaction Care must be taken not to destroy the ligand when washing[13] An alternative scheme using a single-phase reaction system and washing the free ligand away with dilute aqueous sodium hydroxide solution has been proposed[69] The effects of different extractant solvents, pH value of reaction media, and shaking time on recovery were investigated

A detection limit of 2 10^{-11} g of Be was achieved which meant that trace quantities of beryllium in uranium oxide and tap water could be determined

Sample	Be content	Ref 69
NBL 98-6 (U_3O_8)	0 5 μg/g	0 48 $\pm$ 0 04 μg/g
Tap water	5 μg/l (spiked)	4 1 $\pm$ 0 3 μg/l

An interesting inorganic investigation was the use of gas–liquid chromatography to study the rate and equilibrium studies of the reaction between beryllium oxyacetate and beryllium oxypropionate[70][71] The rate curves were described by consideration of the ligand-exchange processes occurring in the system Equilibrium data indicated tht the system shows excellent agreement with the theoretical predictions for a completely random distribution[72], so providing an excellent test of the ability of gas–liquid chromatography to monitor such exchange reactions

Gas chromatographic separations involving chromium β-diketone complexes has been a field of intense activity[73]–[75] A good example was the determination of chromium in human blood serum using chelation with trifluoroacetylacetonate followed by extraction into benzene and gas–liquid chromatography with microwave excited emission detection at 357 9 nm[76] The sensitivity was adequate for the normal level present in serum at 3 ppb The precision of the method was 7 5% for a concentration of 5 16 ng/g of Cr in blood serum[76] The determination of low concentrations of chromium (< 1 μg/l) in complex materials such as sea water has long been a challenge to analytical chemists In general, most techniques require some form of chromium preconcentration which is often not quantitative[77,78] Sub-ppb concentrations of chromium in sea water have been determined by isotope dilution gas chromatography–mass spectrometry[79] The samples were first reduced to ensure all chromium was in the trivalent state, which was then chelated, extracted and concentrated as Cr[tris(trifluoroacetylacetonate)] into hexane Following gas–liquid chromatography, the Cr(trifluoroacetylacetonate)$_2^+$ mass fragments were monitored using a selected-ion monitoring (SIM) mode A precision of within 5% was typical

Chromium concentration in seawater (μg/l)

Isotopic dilution gas chromatography mass spectrometry	Isotope dilution spark source mass spectrometry[80]	Graphite furnace atomic absorption spectroscopy[81]
(i) 0 177 $\pm$ 0 009	0 17 $\pm$ 0 03	0 19 $\pm$ 0 03
(ii) 0 19 $\pm$ 0 01	0 18 $\pm$ 0 01	Not determined

With such powerful instrumental techniques available for comparison purposes, the techniques will in the near future be applied to other elements, for example aluminium Siu *et al*[82] have already shown that the effect of adding small quantities of trifluoroacetylacetone to the helium carrier gas is markedly to reduce the tailing and memory effects of trifluoroacetylacetonate complexes of Al(III), Cr(III) and Fe(III) when subjected to gas–liquid chromatography

As outlined for beryllium, the separations of such metal chelates is robust enough to allow separation of five of the possible reaction products formed between

Cr[tris(trifluoroacetylacetonate)] and Cr[tris(hexafluoroacetonate)], using a capillary porous-layer open tubular column coated with Dexsil 300 GC Only Cr[tris(trifluoro-acetylacetonate)] was unresolved from the solvent peak[83] The concept has been taken a stage further using fused-silica capillary columns were 24 out of the possible 25 rearrangement reaction products formed between Cr[tris(trifluoroacetylacetonate)], Cr[tris(hexafluoroacetonate)] and Cr[tris(2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanediene)] were resolved[84] Mass spectral identification lead to the facile assignment of identities, yields and information on the gas-phase stability of such complexes

For normal "ordinary" elemental analyses slow progress has been made, the two most likely directions being the increasing use of capillary columns[85 86] and the synthesis of highly fluorinated compounds (not based on β-diketones)[86 87] In the former, wall-coated open tubular columns especially fused-silica columns, are proving particularly effective, Sucre and Jennings[85] provided a number of comparison separations of a series of trifluoroacetonates, diethyldithiocarbamates, bis(trifluoro-ethyl)dithiocarbamates, or diisopropylphosphorodithioates using a variety of detectors Both nitrogen-thermionic and flame photometric detectors were effective, the former more sensitive but the latter was more selective The synthesis of the trifluo-roethyldithiocarbamato ligand (as the sodium salt)[86,88,89] has produced a ligand which reacts with a large number of metal ions including Zn, Cd, Cu, Ni, Co, Hg, Pb, Bi, Fe, Pt, Pd, Rh, Sb, Tl, In, Cr and Se, the chelates of which have in general vapour pressures about two orders of magnitude greater than the corresponding diethyldithiocarbamate complex[90] In addition, the trifluoro chelates also appear to be more stable than the diethyl chelates by two orders of magnitude being extracted at lower pH values[91] It is unfortunate that the trifluoroethyldithiocarbamate reagent is not available commercially because it appears to be one of the most powerful reagents in the determination of metal chelates by gas chromatography Similarly the fluorinated Schiff's base reagent, 1,1,1,1',1',1'-hexafluoro-4,4'-(1-methylethane-1,2-diyldiimino)-bis(pent-3-en-2-one)[87] which has been proposed for the analysis of copper, nickel and vanadium noids promise Both ligands must be tested to destruction *versus* more conventional methods because with such wide-spectrum reagents for metals with capillary columns, the opportunity for oligo-elemental analysis is available and maybe useful in situations where highly sophisticated facilities such as inductively coupled plasma–optical emission spectrometry or inductively coupled plasma–mass spectrometry (ICP–MS) are not available Regretfully there will be no glory in the detailed examinations/investigations which will have to be carried out, like some other areas of chemistry, a great deal of the cream (the separation or the quoted detection limit lower than anybody else's) has gone What now remains is the chore of actually making it quantitative and therefore useful The competition of opposing techniques is severe, the opportunity for success is limited and extremely careful choices of situation (i e , what type of sample to be investigated) will have to be made

3 LIQUID CHROMATOGRAPHY

The liquid column chromatographic separation of inorganic species has not developed at the same rate as that of organic species The deficiency in this case is

not due to lack of suitable separation substrates but due to the difficulty of devising suitable detection techniques to monitor inorganic species at trace levels in column effluents Direct photometric detection was difficult because of the low wavelengths (< 220 nm) at which most inorganic species absorb, and usually derivatization was required to render cationic species determinable Refractive index (RI) detection has often been inapplicable to the detection of ions separated by ion-exchange procedures, because of the small difference in refractive index between inorganic ions and the electrolyte–buffer solutions used to bring about the elution of the species Electrochemical detection, although extremely sensitive, is limited in general applicability, because of its great selectivity

Ion-exchange chromatography was the most obvious liquid chromatographic technique to apply to the separation of inorganic species and indeed many elegant separations of inorganic ions, especially cations, have been reported[92–94] Prior to the mid-1970's the majority of such separations were of metal ions determined photometrically[95], after post-column reactions with reagents such as dithizone, or using monitoring of radioactive isotopes[92] The state of the art to that time has been well summarised by Saville[96], while Brinkman[97] and Green[98] have reviewed the use of liquid ion-exchangers in extraction chromatography

The renaissance of interest in column chromatography of metals has arose through the very rapid developments in the production of high-performance support materials and the availability of sensitive detectors which can be coupled directly with the separation column However, as discussed by Schwedt[1] up until 1981 less than 100 papers had been published on the application of high-performance liquid chromatography (HPLC) to inorganic analysis, "of those 100, less than half, were concerned with quantitative and very few with practical applications" The situation as far as published papers has changed rapidly but the comment concerning practical applications still remains The constraints of the classical situation have largely disappeared because the techniques of adsorption, liquid–liquid distribution, ion-exchange as well as reversed-phase and partition chromatography (using chemically bonded phases) are all now available HPLC could be of great importance in trace analysis, especially with the increasing possibilities of coupling the column to element selective as well as sensitive detectors So the technique is not limited to the UV or RI detectors but the advantages of atomic absorption or ICP systems can be exploited For example, Ibrahim et al [99] investigated the determination of tetraalkyllead compounds using HPLC and inductively coupled emission detection The column was 12 cm, 10-μm LiChrosorb RP-2 with a solvent of n-butanol–ethanol–water (15 35 50) at a flow-rate of 1 ml/min at ambient temperature The choice of the mobile phase is critical because many of the organic phases commonly used in HPLC easily extinguish the plasma Detection with a UV-absorbance system was used initially to optimise the HPLC conditions For the ICP system, detection limits of 42 ppb of lead for tetramethyllead (2 ng with a 50 μl column injection) and 212 ppb of lead for tetraethyllead (11 ng with the same volume injection) were achieved Sample of regular and unleaded gasoline were examined for their tetramethyllead and tetraethyllead contents as well as for other lead compounds Krull[100] has made an extremely spirited defence (or affirmation) of the three plasma techniques (microwave-induced, direct current and inductively coupled systems) Even the "aficionado" which he is has to admit that there is still a major problem the minimum detectable limit (MDL)

In general, HPLC detector MDLs must be worse, perhaps by a factor of more than 100 *versus* the direct detector situation, mainly because of the dilution effect present in any HPLC method Krull[100] and others[101-103] have experienced significant losses in detection limits using HPLC–ICP systems ranging from twenty to three orders of magnitude The problem is one of almost incompatibility between the nebulizers available for direct ICP systems and that ideal for HPLC–ICP, which just exacerbates the situation of the notoriously inefficient pneumatic nebulizer Therefore, overall MDLs are still less than adequate for practical applications

The problem stems from the inherent inability of pneumatic nebulizers to equilibrate to the very rapidly changing concentration of analyte which emerges from the HPLC column in an extremely discrete volume (100 μl) since most commercially available ICP nebulizers have very large internal volumes and surface areas The spray chamber devices used in direct current plasma (DCP) and flame atomic absorption spectrometry appear to be a much better interface for the HPLC concept and is probably a major reason why HPLC–DCP detection limits are much better (10^3) than for HPLC–ICP systems The use of a hydride-generation system between the HPLC system and the ICP appears to overcome the problem and allow the achievement of practical MDLs in the range 25–50 ppb for, *e g*, arsenic Obviously, hydride formation is only possible for a limited number of elements and is not a panacea for improved MDLs in HPLC–ICP[100] Continuing with emission spectroscopy, the term replacement ion chromatography (RIC) has been proposed for a new detection system for ion chromatography with the potential of very low detection limits and universal application[104] In this first example, a counter cation associated with an eluting anion is stoichiometrically replaced in a cation-exchange column by a flame photometrically active cation (*e g*, lithium) which is then directed towards a turbulent burner Measurement of the atomic emissions from its replacement ion (Li^+ in the flame is claimed to provide an indirect but quantitative measure of the eluting anion concentration) The reduction in the concentration of free ions in the eluting solvent is crucial to RIC, otherwise detection limits and precision are degraded Cation concentrations may be similarly quantified when the separated sample cations are replaced by Li^+ Detection limits for monovalent ions are reported to be in the low micromolar level The limitations and capabilities of the technique were appraised and possible extensions are considered

A reducing vessel which completes a liquid chromatograph with a cold-vapour atomic absorption spectrometry system has recently been described for the determination of mercuric compounds[105] The system works effectively as a continuous detector, the volatized mercury is swept out by air into a normal cold vapour absorption tube When stannous chloride is used as reductant mercury alkane thiolates are monitored For the detection of inorganic, methyl and ethyl mercuric compounds, sodium borohydride is used The system is reported to have a high sensitivity and specificity due partially to lower matrix interferences than in UV-absorbance detection The role of spectrochemical methods using element-specific detectors in chromatography has recently been reviewed[106,107] Following the initial activity in electrochemical detectors[108-112] there appears to be a lull in development of the subject although the determination of pertechnetate using reductive electrochemical detection has been reported recently[113] Pertechnetate which is frequently used in the preparation of many diagnostic radiopharmaceuticals is generally present in eluents

in the concentration range 5 10^{-8} to 5 10^{-6} M No sample pre-treatment is necessary since impurities and other components are separated using an amino-bonded HPLC column Using either both static mercury drop (SMDE) or solid-state electrode detectors, in conjunction with vigorous deoxygenation procedures, total pertechnetate in effluents is readily determined Severe electrode failing phenomena limited the use of solid electrodes to TcO_4^- concentrations less than 10^{-7} M The working range for a carbon electrode was 8 5 10^{-9} to 1 0   10 M TcO_4^- while for the SMDE it is 2 1 10^{-8} to 1 10^{-4} M

For normal UV–visible absorbance measurements, following HPLC the design of the post-column reactors is critical both with respect to their effect on sensitivity and resolution The most promising post-column reactor type appears to be based on the packed-bed reactor system[114] The choice of post-column reaction detector is greatly influenced by the reaction type A multi-element post-column HPLC detector based on dithizone as a complex-forming reagent has now been reported[115] Heavy metal ions were detected down to nanogram levels, while working ranges up to the microgram level is possible The use of this heavy metal detector which may be tuned by pH control is discussed An advantage of this system for multi-element determinations is that the decrease in the dithizone absorbance at 590 nm is measured rather than the increased absorbance at different wavelengths particular to each metal dithizonate

A simple post-column reactor based on Eriochrome Black T (EBT) has been developed to determine trace metals after separation on a silica-based cation-exchange column[244] Quantitative determination is performed by measuring the decrease in the absorbance of the post-column reactant at 610 nm Quantitative analysis of nine metals in 16 min was achieved Linear calibrations up to 10 $\mu g/g$ for Cd, Co, Cu, In, Fe(III), Fe(II), Mg, Mn, Ni and Zn are possible with limits of detection between 2 and 5 ng The relationship of the cation-exchange chromatography and the organic acid eluent to the post-column reactor was discussed The system was used to determine Co, Cu, Fe, Mn and Ni in standard alloys and the accuracy of the method was shown to be very good with coefficients of variation in the range 1–11% (Tables 2 and 3)

Although there is now only limited effort being placed into paper or thin layer chromatography, interesting work is reported Ohlsson and Huntze[116] have proposed a high-performance thin-layer chromatographic (HPTLC) analysis for organotin compounds in preservative solutions and preservative treated wood The organotin compounds of direct relevance were bis(tri-n-butyltin)oxide (TBTO), tri-n-butyltin naphthanate (TBTN) and their degradation products (dibutyltin and monobutyltin compounds) After extraction from wood with ethanol containing 0 5% (v/v) HCl, separation of the differing types of organotin compounds were achieved on HPTLC silica gel plates using a variety of solvent systems Some 15 to 120 ng of compound being present in a 1-μl injection The sample spots were measured using a scanning densitometer after prior decomposition of the organotin compounds to inorganic tin using UV-irradiation and visualization using Pyrocatechol Violet

Applications of the method to the detection and quantification of organotin compounds in wood preservative solutions, recently impregnated wood, and in wood samples taken from 5-year old window frames are presented The accuracy and precision achieved is very high, the coefficient of variation of six determinations being of the order of 2%

TABLE 2

ANALYSIS OF HYCOMAX III PERMANENT MAGNETIC ALLOY (BSC No 384)

Metal	Found (%, w/w)	Coefficient of variation (%) (n = 8)	Certified value (%)
Cobalt	33 7	1 3	33 7
Copper	3 06	5 2	3 06
Iron	34 6	2 4	
Manganese	0 10	11 5	0 10
Nickel	14 8	4 4	14 6

Similar studies on the determination of silver in aluminium[117] (where the eluting solvent composition was chosen via a Simplex optimisation), iron ion in ferrous sulphate syrups and similar pharmaceutical preparations[118], or the estimation of nickel in some of its alloys[119] have been reported Obviously in preparation for further investigations, a series of cis- and trans-β-diketone complexes of Co(III), Cr(III) and Rh(III) have been separated in either Al_2O_3, SiO_2 or silanised SiO_2 TLC plates[120] High-speed zig-zag scanning densitometry with linearized calibration graphs were used to determine the concentration of complexes Detection limits of between 2 and 8 10^{-6} M for 1 μl sample, with linear calibration graphs from 10^{-5} M to 10^{-3} M with a coefficient of variation of 0 12 to 2 4% were reported A rather novel detection system, photo-acoustic spectroscopy has been proposed for the determination of ultra-trace amounts of metal chelates[121] A combination of proton-induced X-ray emission (PIXE) and TLC has been proposed for elemental analysis in solutions The metals ions were preconcentrated and separated as their chelates with 1-hydroxy-2-pyridinethione or 8-mercaptoquinoline ligands on SiO_2 or Al_2O_3 layers followed by determination using PIXE Calibrations using a series of graduated dilutions and correction for dependence of the PIXE signal intensity on the chromatographic migration length are described[122] The work has since been extended to other chelates and to include UV-reflectance spectroscopy measurements[123] A rapid quantitative separation of the different valency forms of tellurium using TLC layers of Al_2O_3 with 40% (w/w) caustic soda solution as eluent Stannous chloride solution was used as developing reagent The separation was verified using ^{129m}Te and ^{127m}Te radioactive tracers[124]

However, this work is almost insignificant to the intensity of activity now being extended in column chromatography Using the historical concept of chromatography, adsorption, partition (particularly reversed phase), and then ion-exchange separations will be discussed

TABLE 3

ANALYSIS OF MONEL ALLOY 400 (BSC No 363/1)

Metal	Found (%, w/w)	Coefficient of variation (%) (n = 8)	Certified value (%)
Cobalt	0 033	8 3	0 032
Copper	31 5	3 0	31 9
Iron	1 73	9 2	1 86
Manganese	1 17	9 4	1 26
Nickel	64 2	1 6	64 7

The amenability of metal chelates has led many workers to develop adsorption (or normal-phase) chromatography with UV–visible spectrophotometric detection In particular the dithiocarbamates have received much attention[125–128] Thus the separation of some nine metals as their diethyldithiocarbamates using LiChrosorb Si-60 (10 μm) with a mobile phase of 10% chloroform in cyclohexane with detection at 254 nm was reported[127] The metals included such important ones as Cd, Co, Cr, Cu, Pb, Mn, Ni and quantitative analyses were to be published later (Perhaps the reviewer is being unkind but my searches tell me "later" never arrived') Similar work was reported by Heizmann and Ballschmiter[129] but using diethoxyethyldithiocarbamates while O'Laughlin and O'Brien[128] also investigated dithizone as a pre-column preparation reagent Columns of μPorasil (10 μm) with toluene as a mobile phase at flow-rates of about 1 ml/min with detection limits between 5 and 10 ng are tabulated Other sulphur-containing ligands, such as 8-mercaptoquinoline and 1-hydroxypyridine-2-thione have been employed, the former in the separation of chelates of Fe, Co and Ni, the latter for Ni, Pd, Pt, Rh and Ir, using a LiChrosorb SI-100 (10 μm) column[130] The mobile phase being dichloromethane containing 0 5 or 5% tetrahydrofuran Detection was at 270 nm for the 8-mercaptoquinoline and 254 nm for the 1-hydroxypyridine derivatives However, attainment of quantitative results is not possible probably due to decomposition of chelates during elution Eggers and Russel[131] reported that the chromatographic behaviour of As(III), Sb(III), Bi(III), Se(II), Te(II) and Ni(II) as xanthate complexes was seriously affected by decomposition effects Polar stationary and mobile phases acting as Lewis bases caused decomposition of the complexes by displacing the xanthate ligands Separation without decomposition was possible with reversed-phase systems when using the cyano- and diol-modified columns Such problems have led to proposals on the workable criteria for the chromatography of metal chelates[132] An intriguing study of the HPLC of the metal chelates of dialkyldithiophosphoric acids has been very recently reported[133] Thus mixtures of any two dialkyldithiophosphate chelates of Co(III) readily undergo ligand exchange in solution and four peaks were resolved by adsorption chromatography using Spherisorb silica 5 μm (S5W) Under more vigorous conditions the similar (but inert) Cr(III) chelates can be prevailed upon to react The identities of the mixed ligand chelates have been established by mass spectrometry[134,135] Mixtures of three chelates gave rise to ten species, one of which has been attributed to a mixed-ligand chelate containing the three different ligands, A = iso-$(C_4H_9O)_2PS_2^-$, B = iso-$(C_3H_7O)_2PS_2^-$, C = $(C_2H_5O)_2PS_2^-$, with the retention factors (k') ranging from 0 6 for MA$_3$ to 5 3 for MC$_3$, with MABC k' = 2 1

For quantitative determinations, a particularly promising approach to liquid chromatographic multi-element determinations involves pre-column formation of chelates (in a multi-element sample) followed by reversed-phase liquid chromatographic separation of the chelates There is already a small literature on dithiocarbamic acids[136–139], β-ketones[140], 8-hydroxyquinoline[141] and β-ketoamines[142,143] Some of the interesting work in dithiocarbamic acids seems to have arisen from the realisation that such complexes are capable of being involved in oxidation/reduction sequences Thus Bond and Wallace[144] produced a procedure for the specific determination of copper(II) based on reversed-phase liquid chromatography using a C_{18} silica based column and acetonitrile–water mixtures as mobile phase A dithiocarbamate salt was included in the mobile phase and aqueous solutions injected to form

the copper–dithiocarbamate complex *"in situ"*, alternatively external formation of the complex followed by injection on to the column was employed The eluted Cu(dithiocarbamate)$_2$ complex undergoes a reversible one-electron step reduction/oxidation step at Pt, Au or glassy carbon electrodes in acetonitrile-water medium enabling copper to be determined down to a level of 1 ng Interference effects were examined for some 20 ionic species and at the 10-fold excess (by weight) no interferences were noted Such studies indicated that multi-element analyses were possible since many other elements are also electroactive The work was extended to the determination of Cu, Ni, Co, Cr(II) and Cr(VI) ions[136] Exploiting electrochemical detection at Au, Pt or glassy carbon electrode surfaces, many different cells, modes of complex formation and detection format were examined to provide optimisation of the technique Limits of detection substantially less than 1 ng were obtained for all metals For the simultaneous determination of all five species, external formation of complexes prior to injection is essential However, for the rapid determination of only Cu and Ni, the dithiocarbamate ligand may be included in the mobile phase with *"in situ"* complex formation The work has now resulted in the development of an automated system capable of determining copper and nickel by reversed-phase liquid chromatography with electrochemical and spectrophotometric detection[137] The resulting comparison of atomic absorption spectrometry (batch process) with liquid chromatography with either electrochemical or spectrophotometric detection for a series of refinery samples is detailed and impressive Surely this is the way how liquid chromatography should develop!

A method of simultaneously determining Cr(III) and Cr(IV) based on a similar reaction was proposed some time ago[145] Schwedt[146 147] suggested the use of diethyl- or tetramethylenedithiocarbamates and reversed-phase liquid chromatography for the analyses of heavy metal ions present in water Smith and his colleagues[148,149] separated a series of heavy metal diethyldithiocarbamates on a Hypersil ODS column with an eluent containing sodium diethyldithiocarbamate Lead ions have been examined in more detail and to obtain reproducible results the mobile phase must contain chloroform to prevent precipitation of the chelate A comparison of gas–liquid chromatography and reversed-phase HPLC for the determination of Cd in biological materials has recently been published[150 151] Optimum conditions for chelation and extraction of metal ions were at pH 4 5 with Pb(II) as internal standard with chloroform containing 1% (w/w) sodium diethyldithiocarbamate After separation of the chloroform layer, the organic phase was removed and the residue dissolved in ethyl acetate Gas–liquid chromatography was accomplished using 5% (w/w) OV-101 on Chromosorb W HP with a flow-rate of 23 ml/min helium, and a temperature programme from 230 to 250°C at 10°C/min The flame ionization detector and N-selective detector as well as mass spectrometry were used to identify the chelates Cadmium was determined in liver and kidney (after ashing with 65% HNO_3 in a PTFE bomb at 120°C for 3 h) with a coefficient of variation of $<2\%$ The results also compared with those using atomic absorption spectrometry The chelates of Fe, Zn, Cu, Hg and Co did not interfere and the chelates could be identified by their respective retention times In a similar study but determining both Cd and Pb in biological material, Pd(II) was used as the internal standard Reversed-phase HPLC was employed using a C_8 LiChrosorb column with methanol–water–chloroform (2 1 1) as mobile phase and monitoring at 270 nm While Tl(I) interfered with the Pb(II) determination, other heavy metals caused no problems

A similar approach uses a new, very stable dithiocarbamate, namely [bis(*n*-butyl-2-naphthylmethyldithiocarbamate)Zn(II)] which has been synthesised and its use in trace metal determinations is being pursued[152] The metal complexes formed by this ligand are very stable and kinetically inert even at 1 10^{-8} *M* level Various metal complexes including Fe(III), Cu, Hg, and Co have been "baseline" separated using a C_{18} reversed-phase HPLC column, with methanol–water (96 5) containing 1 0 m*M* Tris buffer adjusted to pH 8 25 by addition of H_3PO_4 Detection limits approaching 12 ng using a variable-wavelength absorbance detector are claimed Calibration graphs were linear, at 10^{-6} *M* or less a precision of better than 2% was achieved Using the detection limit concept of Habaux and Vos[153] the limits of detection criteria were Hg(II) 3 ng, Cu(II) 1 ng and Fe(III) 10 ng This is a pleasing feature because it is one of very few papers where a meaningful and reproducible (in a statistical sense) detection limit is quoted Obviously the naphthyl groups impart high absorptivity to the complex while the combination of bulky naphthyl and *n*-butyl groups appears to stabilise the metal chelates But real samples have yet to be determined —"this preliminary recovery study demonstrates the possibility of pre-concentrating trace metals from real samples provided that other organic matter in the sample does not interfere with the formation of the metal complexes" is the phrase to be quoted from the end of the paper One intriguing aspect of the work is that the total retention factor (*k'*) varied dramatically with a given mobile phase as the column nature was varied It was tentatively inferred that the complexes are interacting (in part) with the free silanol groups because very heavily loaded (22%, w/w, C) C_8 reversed-phase columns gave very poor selectivity and diminished retention

Cobalt(II) as chelate complex with 3-mercapto-1,5-diphenylformazan was separated from Cd, Ni, Pb and Zn chelates using a Zorbax ODS column and methanol–water (85 15) as the mobile phase[154] Using peak area integration the concentration range 5 2–30 ng resulted in linear graphs even in the presence of Cd, Ni, Pb and Zn The total analysis time was of the order of 25 min Naturally selenium can be determined as the piazaselenols using LiChrosorb RP-8 with methanol–water (4 1) as mobile phase The limit of detection with 5-chloro-1,3-benzoselenadiazole was 1 6 ng of Se The method was employed to determine selenium in potable, surface and waste waters respectively[155]

The possibilities of the separation and the limits of detection of metal 1-(2-pyridylazo)-2-naphthol (PAN) chelate complexes in reversed-phase mode by both HPLC and TLC were investigated sytematically[156] Only the complexes of Cu, Co, Ni or Cu, Fe and Co as mixtures were separable All other metal complexes showed instability in reversed-phase systems The best conditions for separation were using RP-2 type material, with a mobile phase of acetonitrile–water–citrate buffer pH 5 0 (80 18 2) containing 0 01 *M* ammonium thiocyanate A similar study using pyridyl azo naphthol complexes of Co(III), Fe(III) and Ni(II) has been reported[157] The procedure involved pre-column preparation of the chelates by boiling the metal containing solution plus the ligand in ethanol and extracting the resultant cooled mixture with chloroform Elution was effected by using *n*-hexane–chloroform–ethanol (4 1 5) as mobile phase with detection at 520–560 nm The detection limits were Fe 0 05 μg/ml, Ni 0 13 μg/ml and Co 0 3 μg/ml as metal Large amounts of Cd, Cr(III), Hg(II), Mn and Zn did not interfere From PAN to 4-(2-pyridylazo)resorcinol (PAR)

is not a big step and Roston[158] has demonstrated that using pre-column chelation with PAR, liquid chromatographic determinations of Cu, Co, Ni and Fe as PAR-chelates at the ppb level are feasible Isocratic elution was employed with 65% 0 1 M pH 6 5 $NH_4H_2PO_4$–$(NH_4)_2HPO_4$ buffer, 35% distilled methanol on a 5-μm Bio-phase ODS column Both fixed-wavelength UV absorption (254 nm) and oxidative thin-layer amperometric detection have been investigated Response linearity, detection limits and the analysis of natural water samples were carried out Typical detection limits (UV first, followed by amperometry) are Cu (0 34, 0 74), Co (0 06, 0 02), Ni (1 2, 0 83), Fe (1 2, 0 93) Such a preliminary investigation can only be the beginning of a series of investigations which will doubtless include different bonded phases as the stationary phase, gradient mobile phase delivery and the additional metal ions with which PAR can react

It is pleasing for the reviewer to note the publication of the last three papers, using as ligands compounds which he has had a role to play in their development Frankly there are many others some based on the thiazolyl system [such as 4-(2-thiazolylazo)-resorcinol (TAR) and 1-(2-thiazolylazo)-2-naphthol (TAN)] which may be even better as pre-column derivatizing agents[159] It was always the intention of the late Dr F H Pollard that this is how these versatile reagents should be used However, before any of the methods of reagents are to provide serious competition for multi-element determination procedures utilizing the full panoply of statistical procedures recommended by Cardone[160,161] and Hunter[162] have to be implemented Perhaps as inorganic analytical chemists interested in trace analysis we must take a leaf from the book published by the pharmaceutical/therapeutic or pesticide residue chemists If not, a wonderful opportunity will have been missed For example, data for the following investigation may be fascinating to process in this manner The simultaneous determination of metal ions by HPLC of water-soluble porphyrin–metal complexes has been suggested The simultaneous spectrophotometric determination of 10^{-9}–10^{-8} g/ml levels of Cu, Zn and Pd by HPLC with α-, β-, γ- and δ-tetrakis(1-methylpyridinium-4-yl)porphine (TMPyP) was developed[163] Molar absorptivities, $\varepsilon(cm^{-1}\ M^{-1})$ for the complexes at 430 nm were 1 88 10^5 (Cu), 1 88 10^5 (Zn) and 0 64 10^5 (Pd), calibration curves were linear over the range 0–0 08 μg/ml, with coefficients of variation (5 determinations) of 0 95% for Cu, 2 02% for Zn and 3 57% for Pd Similarly HPLC of rare earth metals followed by post-column colour reaction with Arsenazo III has been proposed[164] Aqueous lactic acid was used as the mobile phase, fortunately the colour reaction is not affected by large amounts of lactate Two intriguing papers have recently been published which discuss the analyses of platinum anticancer drugs using liquid chromatography–electrochemical detection (LC–ED)[165] or a post-column reaction detector[166] The LC–ED investigations has led to the successful determination of at least three separate platinum anticancer (neoplastic) agents (1) cis-dichlorodiammine Pt (cis-Pt), (2) cis-diammine-1,1-cyclobutane dicarboxylate Pt (CBDCA), and (3) cis-dichloro-trans-dihydroxy diisopropylamine Pt (CHIP)

The parent compound, cis-platin (CDDP) maybe determined via both oxidative and reductive LC–ED, with differences only in the limit of detection Calibration plots and minimum detectable limits have been determined for all three derivatives Both CBDCA and CHIP can be determined by direct LC–ED, but the MDL for CBDCA is not sufficiently low for practical stability or clinical studies A new method

of derivitization for CBDCA and related platinum compounds has been developed, wherein they are quantitatively converted to cis-Pt and the final derivative is then determined as for the parent cis-platin (CDDP) CDDP can be determined via reductive LC–ED at the 100 ppb level in plasma The final methods of LC–ED studies have now been applied to a variety of stability studies with all three Pt drugs, in water, plasma and saline infusion solutions It is suggested that these LC–ED methods are now directly applicable to "real world" clinical settings and cancer patient samples The column used is an reversed-phase C_{18} column (10 μm, 25 cm × 4 6 mm I D) with hexadecyltrimethyl ammonium bromide (HTAB) as ion-pairing agent in an 0 01 M acetate buffer pH 4 6 containing 0 15 mM HTAB The current mostly accepted analytical procedure for CDDP quantitation is HPLC separation[167–170] followed by off-line quantitation of the Pt in each fraction using electrothermal atomic absorption spectrometry[171,172] Recently, on-line LC–ED has been used for the quantitation of both CDDP and CHIP in urine samples but the method was not responsive to the other platinum antineoplastic agents investigated[173,174] Therefore, a spectrophotometric monitoring method was preferred but due to the very poor molar extinction coefficients of Pt(II) complexes a derivatization procedure was required Nucleophiles which react rapidly with Pt(II) compounds should convert a variety of Pt compounds (of differing ligand composition) to a final common product[175] However, to maintain the selectivity of the system, a chromatographic separation of the solutes must preceed this reaction[176,177] Based on the work of Hussain et al [178] a post-column reaction detector sensitive to Pt(II) complexes was presented[166] in which sodium bisulphite is used as derivatizing agent with $K_2Cr_2O_7$ as an activating agent The influences of mobile phase changes (i e , pH, organic modifiers, electrolytes), oxygen, other metal ions, and order of reagent addition on the reaction kinetics and product yield were defined and used to optimise the detector response

Detection at 290 nm resulted in an on-line post-column sensitivity of 40–60 ng/ml for selected cis-dichloro platinum complexes with a sensitivity of 300–1200 ng/ml for four substituted malonatoplatinum complexes The system was used to monitor the degradation of CDDP and to quantify CDDP degradation in plasma Since the sensitivity of the reaction in plasma was comparable to that achieved using HPLC–off-line electrothermal atomic absorption spectroscopy, significant utility for the post-column reactor in chemical analysis is suggested

4 ION CHROMATOGRAPHY

Turning to ion chromatography, the reviewer will only discuss those separations which lead to a determination The spectrophotometric determination of boron after separation of the boron–chromotropic acid complex and the excess of chromotropic acid was achieved by means of reversed-phase chromatography[179] The mobile phase consisted of 48% methanol and 52% deionised water containing 1 1 10^{-2} M $(C_4H_9)_4N^+Br^-$ and 5 10^{-3} M phosphate buffer at pH 8 5, the column was 5 μm ODS, with detection at 350 nm Although the ligand and boron–ligand complex have the same spectrum, the reaction can be satisfactorily used for the determination of B because the complex is very stable and can be separated from the ligand The merits of the method are (i) the pH range for complex formation is wide, (ii) the complex formed is very stable, (iii) the reaction time for complex formation is very short, and

(iv) co-existing ions scarcely interfere with complex formation or other interfering metal ions are easily masked with EDTA The method has been applied to the determination of boron in (a) hot spring waters which ranged from 30 to 2470 ppb, (b) seawater about 4000 ppb or (c) tapwater 8 2 ppb The results were compared with those determined using 2,6-dihydroxybenzoic acid–Malachite Green as a conventional colorimetric reagent[180]

Since its introduction in 1975, ion chromatography[181] has gained extremely wide acceptance as the method of choice for the determination of in the main inorganic anions[182] Indeed the last three years has seen a tremendous growth in the applications of ion chromatography Originally the suppressed approach was dominant but the published results on non-suppressed column technique has seen a most rapid growth since conventional LC equipment can be used However, newer suppression techniques, e g packed hollow-fibre suppressors[183] and improved columns[184] have maintained interest in the suppressed ion chromatography approach Of some 98 recent applications of ion chromatography only ten could be construed as being involved with metal determinations Only four papers dealt with cations[185–188], the others being separations of anions containing metals e g molybdate[189,190] or tungstate[189] For example, As, Cr, Mo and W as the XO_4^- anion have been determined by ion chromatography after treatment of a suitable aqueous solution of the anions with hydrogen peroxide at alkaline pH[191] The anions were separated in about 25 min by using as eluent 0 005 M Na_2CO_3 solution using conventional equipment Detection limits were improved by using a preconcentration device The method was used for the analysis of natural as well as waste waters Selenium as SeO_4^{2-} could also be separated from the analytes by using 0 003 M Na_2CO_3 as eluent but then the total time of length of run (determined by elution of CrO_4^{2-}) was 45 min The process has been taken a stage further by Hoover and Yager[192] who have determined very low levels of selenite, selenate and arsenate by separation from chloride, bromide and sulphate in surface, drinking and groundwaters with statistical detection limits of between 0 02 and 1 2 μg of trace element depending on the minor element to be separated and on the actual type of water matrix Recycling techniques were used to isolate and concentrate the sample prior to actual determination

The alkali metals, Na^+, NH_4^+, K^+ have been determined in a tertiary effluent using ion chromatography with electrical conductivity measurements The results were comparable with those achieved using flame emission and atomic absorption spectroscopy[193] Instead of the normal conductivity or direct UV absorption detection, for the determination of transition and rare earth metals, a postcolumn reactor using PAR or Arsenazo I respectively has been proposed[194] So using a 0 1 M sodium lactate solution (pH 4 5) separations of Mn, Fe, Co, Cu, Ni, Cd and Zn were achieved Using PAR as detecting system at 498 nm A gradient elution system increasing from 0 01 to 0 04 M 2-methyllactic acid separated Lu to La

Columns other than normal ion exchangers can also be used for the technique of ion chromatography, so getting away from one of the major problems, the cost of organic polymer columns[195] Thus Molnár et al[196] separated Na^+, K^+, NH_4^+ and Ca^{2+} on a reversed-phase C_{18} column using secondary equilibria and conductivity detection Skelly[197] expanded the work, with a reversed-phase column and adding octyl amine salts of mineral acids to separate a large number of anions He

attributed the mechanism to ion exchange rather than to partitioning via ion pairs Cassidy and Elchuk[198] then used dynamically coated columns using hydrophobic molecules containing ionic functional groups in the eluent to separate different cations Thus C_{12} or C_{20} sulphate or C_6 or C_8 sulphonates were employed The metals once separated were determined by post-column reaction with PAR The potential of this approach for the preparation of ion exchangers of variable capacity and infinite selectivity is discussed and some of the associated analytical aspects were briefly examined This particular paper probably holds the key to all viable determination of metals by ion chromatography Certainly such dynamically coated systems offer superior resolution of transition metal ions and greater flexibility with regard to choice of separation conditions than conventional bonded exchangers Using both permanently bonded and dynamically coated columns for comparison purposes Cassidy and Elchuk were able to separate a large variety of anions[199] However, the use of HPLC and the use of ^{139}La as a fission monitor have been examined for the determination of a number of fissions and "burn-up" in $(ThU)O_2$ fuels The fission product ^{139}La in a solution of irradiated fuel was separated on a reversed-phase column dynamically modified with 1-octanesulphonate The eluted metal ions were monitored with an "on-line" post-column reactor system using either PAR at 535 nm or Arsenazo III at 653 nm[200] The present HPLC procedures which have been described for the determination of fission monitor[201-203] have all involved collection of fractions and subsequent determination by mass spectrometry Using this HPLC approach, the relative standard deviation of peak heights for La in 13 fuel solutions over a period of a month was 0 96% The agreement between HPLC and those results obtained by standard mass spectrometric techniques was 0 1% The limit of detection for PAR with rare earths is 5 ng but too high a pH value is required for the reaction because at this pH, ThO_2 precipitates out However, with the Arsenazo III reaction at pH 2 5, the detection limit is 2 5 ng

An extremely attractive feature of the dynamic systems is the ability to adjust the effective ion-exchange capacity of the column with changing the concentration of sulphonate modifier in the eluent, and can lead to dramatic changes in selectivity Thus with 0 01 M 1-octanesulphonate, Th and U are eluted in the middle of the rare-earth group of elements, but using 0 00011 M octanesulphonate all the rare earths are eluted prior to Th and U even when the combined (Th + U)/rare earth ratio was 2000 1 Because the mass transfer is very rapid for these dynamically coated columns, the effective ion-exchange capacity can be altered in only a few minutes The height equivalent to a theoretical plate for rare earths was of the order of 0 02–0 03 mm at linear column velocities of 3 3 mm sec^{-1} Sharp and symmetrical peaks were obtained for actinides such as U, Th, Pu and Am, all of which usually give broad, tailing peaks with ion exchangers

Similarly to the determination of La, the U and Th in fuel solutions can also be measured Both elements give well-defined separated peaks, with linear calibration graphs Comparison of various uranium containing samples by this HPLC system and by coulometry produced agreement to within 0 3%, while the coefficient of variation of differences between analyses was 0 9% Application of HPLC to the determination of heavy elements in UO_2, $(ThU)O_2$, $(U,Pu)O_2$ fuels and "burn-up" in UO_2 and $(U,Pu)O_2$ fuels is under investigation

The scope of ion chromatography using a conductivity detector has also been

expanded to include several additional divalent metal ions and the trivalent lanthanide cations[204] The resins used are lightly sulphonated polymers probably based on RP-1 and a complexing anion is incorporated into the eluent which increases the number of metal ions which may be separated and improves the sharpness of the eluted peaks Further selectivity was achieved by also adding a complexing agent to the sample and then eluting with an eluent containing ethylenediammonium tartrate Thus the following separations were achieved

(i) Zn, Co, Mn, Cd, Cu and Sr using 1 10^{-3} M ethylenediamine plus 1 10^{-7} M tartrate at pH 4

(ii) The seven heaviest lanthanides (Lu to Tb) using 3 10^{-3} M ethylenediamine plus 3 10^{-3} M α-hydroxyisobutyrate

(iii) Mg, Ca and Sr with 4 10^{-3} M ethylenediamine plus 3 10^{-3} M tartrate at pH 4 5

Indeed the technique provided a rapid and selective method for the first three alkaline-earth cations in a variety of samples

With the rise in the use of the UV-absorbance detector, possibly a report on the possibility of employing the detector in quantitative ion chromatography without standard is necessary[205] Samples of ions were studied by non-suppressed ion chromatography and a UV detector When two eluents of similar properties but different absorptivities at normal concentration are used in succession, two distinct chromatograms are obtained for the same sample The information can be used to predict the number of equivalents of each ion present as well as its absorptivity In conjunction with elution time studies, molar concentrations can also be obtained The procedure does not require knowledge of the identity or any physical properties of the ionic species

Although not ion chromatography, the chromatographic behaviour of alkali and alkaline earth metal halides on crown ether-modified silicas has been investigated with water or water–methanol mixtures as the mobile phase Alkali metal halides MX (X = Cl, Br or I) can be successfully separated on poly(benzo-15-crown-5) and bis(benzo-15-crown-5) modified silicas[206]

The area of extraction chromatography has not received much attention recently since a review in 1983 cited some sixteen references[207] The elution and spectrophotometric determination of gold after its separation from non-volatile platinum metals using column extraction chromatography[208] The column was silica treated with tri-n-octylamine, a mixture of 2 25 M hydrochloric acid and 5 M nitric acid was used for elution of iridium, while the gold was eluted together with tri-n-octylamine by acetone The chloroaurate was converted to the bromoaurate and determined photometrically at 394 nm An interesting example of the use of extraction chromatography was the determination of iron present in multicomponent glasses used for optical fibres[209] Graphite powder was used as solid support and its usage to determine the iron without elution from the column The detection limit was 4 $10^{-6}\%$

A microprocessor controlled system for the radiochemical separation of individual rare earths from mixed fission products has been developed[210] The chemical separations are achieved in two HPLC columns coupled in series The initial column separates the rare-earth group by extraction chromatography using dihexyldiethylcarbamylmethylphosphonate adsorbed onto Vydac C_8 RP resin The second column

which isolated the individual rare earths was Aminex A-9 using α-hydroxyisobutyric acid Both the lanthanide group[211] and the actinide group[212,213] have been determined using extraction chromatography Martella et al [212] compared the efficiencies of anion-exchange, solvent extraction and extraction chromatography for reducing the plutonium and americium levels in nitric acid waste to levels below 1 10^{-1} g l^{-1}

The retention of various transition metals on a silica gel column treated with a mixture of Aliquat 336 and Thorin I in chloroform decreased in the order Ni > Co > Fe(III) > Cu, Mn, Cd, Zn Ni, Co and Fe(III) are well separated from each other and from other weakly adsorbed metals[214]

5 ION-EXCHANGE CHROMATOGRAPHY

A major review on ion-exchange chromatography has recently been published testifying to the general interest in this area of chromatography[215] The search for new and more inert polymer packings has led to modified fluorocarbon polymer, phenyl Kel-F being functionalised to form strong cation- and strong anion-exchange HPLC packings[216] The effects of pH, ionic strength and mobile phase counter-ion on the solute retention were studied to indicate the presence of the ion-exchange process Separations of inorganic cations (Li^+, Rb^+, Mg^{2+}) using 9 10^{-4} M $CuSO_4$ as eluent were carried out, but the retention time for Mg^{2+} was in excess of 90 min However, these packings also exhibit reversed-phase characteristics Alteration of the pH of the mobile phase was found to control the retention mechanism of the ion-exchange reaction The permeability of both types of columns was good, operating pressures of only 700 p s i being needed for a flow of 1 ml min^{-1} for a water–methanol (50 50) mixture

Two oxidation procedures for the synthesis of silica gel-based aliphatic sulphonic acid cation-exchange resins for HPLC have been reported[217] Several reaction conditions for oxidising terminally bonded thiols with organic peroxides are provided with yields, capacities, reproducibility and chromatographic behaviour The maximum capacity achieved was 0 34 mequiv /g The advantages of silica-based hydrolytically stable supports containing metal-complexing ligands has been stressed by Gimpel and Unger[218,219] A silica of 14 nm pore size was reacted by two procedures to produce a series of complexing silanes based on the aminodiacetic acid grouping Calculations showed that the surface average of the polymeric support is a rather thin layer which agreed with kinetic performance data The advantages of this material are pressure stability, no swelling no hydrophobic interactions and a fast transfer rate Obviously such materials are open for considerable exploitation

Metal ions were shown to be retained on a silica column from an aqueous mobile phase by cation exchange[220] The major mobile phase variables evaluated included mobile phase pH, ionic strength, mobile phase composition, type and concentration of counter-ion, inorganic analyte concentration and the use of complexing agents as mobile phase additives Chromatographic conditions for the separation of alkali metals, alkaline earths and several rare earth metals are discussed For the separation of magnesium and calcium on Zorbax Sil, methanol–water (1 4) mobile phase containing 3 0 10^{-3} M sodium citrate at pH 7 41 was used

Also of interest are the measurements of a reversed-phase column's capacity for hydrogen ions which was about 9 μmol[221] Measurements of the displacement

of H^+ from the column material by Na^+ were consistent with anion-exchange process Breakthrough capacities of alkali metals were in the 10–15 μmole region in a mobile phase consisting of methanol–water (55 45) plus 5% 0 1 M H_3BO_3 (pH 5 37) The break-through curves were typical of the behaviour of a cation-exchange material The cation-exchange distribution coefficients of the alkaline earth metals have been measured on insoluble hydrous titanium dioxide fibres $H_2Ti_4O_9$ xH_2O at 298°K as a function of pH in the range 1–4 The adsorption behaviour of these ions is well explained by their ion-exchange reactions with H^+ within the fibre[222] A separation of strontium(II) from barium(II) was achieved on these fibres using aqueous hydrochloric acid as eluent

Trace amounts of up to 1 5 mg of gallium(III) can be separated from up to gram amounts of Al, Cd, Cu, In, Mn, Ni, Pb, U(VI) and many other elements by eluting these elements with 8 0 M hydrochloric acid from a column containing 13 0 ml (3 0 g) of AG 50W-X4 cation-exchange resin of 100–200 mesh particle size in the H^+ form[223] Gallium can be separated from up to 2 g of iron(II) and up to 10 mg of scandium by eluting the iron with 8 0 M hydrochloric acid containing 0 30% (w/w) titanium(III) chloride and eluting the scandium with 7 0 M hydrochloric acid The retained gallium(III) is eluted with 2 5 M hydrochloric acid, the separations are sharp and quantitative

One of the major problems in the chromatography of radioactive solutions is the decomposition of the eluent[224], so gradient elution has been proposed as a method of overcoming this difficulty As a treatment of low adsorbed doses, the use of gradient elution was very successful. but for high adsorbed doses, a separation was not achieved owing to radiolysis of the eluent even with gradient elution

On Bio-Rad AG1-X8 anion-exchange resin (200–400 mesh), palladium and platinum were separated by elution with 0 2 and 5 M perchloric acid, respectively[225] If gold is present, then it is retained by adding 0 003 M hydrochloric acid to the eluent Alternatively, reduction using bisulphite enables the elution of platinum(II) with 6 M hydrochloric acid before recovery of palladium(II) with 0 2 M perchloric acid Any iridium(IV) present is also reduced to iridium(III) and can be eluted ahead of the platinum(II) by using 2 M hydrochloric acid

The speciation and quantification of arsenate, arsenite, selenate and selenite was achieved via the use of anion-exchange HPLC and sequential ICP determination[226] Since the spectrometer for sequential ICP detection is considerably less complex than its polychromator counter-part, costs on expensive instrumentation is saved However, the approach is also much more demanding on the chromatography since it monitors only one channel at a time Kinetic detection limits were 1 8 ng As/sec, and 3 9 ng Se/sec while absolute detection limits were 52 ng As(III), 140 ng Se(IV), 57 ng As(V) and 91 ng Se(VI) Reproducibility at the 2 8-μg level was 4, 7, 6 and 6%, respectively, with a linear response through to 9 μg for the lower oxidation states and 5 μg for higher oxidation species

Although not strictly in sequence, the trace analysis and speciation of Cr(VI) and Cr(III) [it is not clear here which Cr(III) complexes were separated or the mechanism of their separation] via HPLC and direct-current plasma emission spectroscopy has been reported[227] The HPLC separation of both chromium species was readily accomplished using ion-pair, reversed-phase conditions, using either $(C_4H_9)_4N^+$ or a camphor sulphonate counter ion in solution The order of elution of the two chro-

mium valencies is completely reversed in going from one counter-ion to the other within the mobile phase It is possible using HPLC–DCP to obtain detection limits for both Cr species in the range 5 to 10 ppb with at least three orders of linearity in the calibration graph The methods were applied to a number of spiked water samples, an NBS chromium water standard, several environmental water samples, various biological samples from the Atlantic Ocean and two Maine tannery samples It appears that this method of analysis is appropriate and applicable to most situations where chromium contamination may be a known or suspected problem

6 GEL PERMEATION CHROMATOGRAPHY

Finally a developing field and one full of interest is that of gel permeation as applied to metals, particularly organometallic complexes or polymeric compounds For example, very recently, four heavy crude oils, Boscan, Cerro Negro, Wilmington and Prudhoe Bay were examined by HPLC and graphite-furnace atomic absorption spectrometry to provide both a vanadium fingerprint and molecular weight characterisation[228] An attempt was made to speciate the vanadium porphyrin and non-porphyrin type compounds by comparison of their size-exclusion and polyamino group HPLC column profiles A number of separated vanadium histograms linked to authentic compounds were presented The gel chromatographic behaviour of trace amounts of Cr(VI) and hydrolyzed Cr(III) in aqueous solution has been studied[229] Similarly gel permeation chromatography has been employed to study the molecular weight distribution of boron–siloxane polymers[230] Analysis of the hydrolyzed B-containing samples showed that the boron was not incorporated into siloxane chain but was attached at the chain ends The size exclusion chromatographic behaviour of six β-diketones and their corresponding Be(II) and Cr(III) complexes in poly(vinyl acetate) gel–organic solvent systems[231] has been studied on the basis of the Ogston[232]–Laurent[233] model The relationship between the distribution coefficient and the molar volume is strongly dependent on the type of substituent in the β-diketone and eluent solvent and cannot be explained merely by a size exclusion mechanism for all the system studied However, the linear relationships between $(-\ln K_{av})^{\frac{1}{2}}$ and V_m (ref 13) in the Fractogel PVA-2000 and p-dioxane system allows the effective size of a given metal chelate dissolved in p-dioxane to be estimated from the K_{av} values of the related free ligand and metal chelates Similarly the speciation of copper in aquatic humic matter has been studied using reversed-phase HPLC with off-line flameless atomic absorption spectrometer as a monitoring system[234]

Reversed-phase liquid chromatography was used for the isolation of dissolved organic matter and dissolved copper–organic complexes from the estuarine waters of Narragansett Bay, Rhode Island[235] The procedure isolated 10 to 30% of the organic matter and up to 50% of the total dissolved copper from various Bay samples

The chromatograms obtained by reversed-phase HPLC of the isolated organic matter showed qualitative differences between sampling stations

A very intriguing paper has recently been published which describes the distribution of zinc amongst human serum proteins using affinity chromatography and ETAAS[236] The serum proteins were albumin and globulin found in human serum The procedure is both simple and rapid, it requires only 400 μl serum for duplicate analyses There is no alteration in the distribution of the zinc between albumin and

the globulins during the separation process and total recovery of zinc is quantitative (ca 98 6%) Albumin-bound zinc and globulin-bound zinc were determined with relative standard deviations of 4 5% and 5 9%, respectively The distribution of zinc obtained in this manner is in very good agreement with that found using more complex techniques The method has one great advantage over other methods such as the poly(ethylene glycol) precipitation technique where the α_2-macroglobulin-bound zinc value is derived from the difference between albumin-bound zinc and total serum zinc

The sensitivity is sufficient to allow an investigation of zinc transport in human serum taken from children The method is needed because other methods are mainly associated with disruption of the interaction between zinc and its carrier proteins Surely this publication will set a precedent for many others to follow and is the forerunner of many such articles

The use of reversed-phase HPLC techniques with molecular and atomic absorption detectors to determine organocopper complexes in soil-pore water has been described[237] Polar dissolved organic compounds and associated copper complexes were separated using a single Hypersil ODS column or two Hypersil ODS columns and a Hamilton PRP-1 column in series Quantitation was achieved using UV detectors for the organic molecule species and graphite-furnace atomic absorption spectrometry for the copper The methods are being used in studying metal associations in soils in the Tamar Valley (an area of heavy mining in the 18th and 19th centuries)

An experimental approach to speciation of heavy metals in soil extracts has been developed[238] The proposed methodology differentiates between differently charged metal species in water and ammonium acetate soil extracts Furthermore a distinction has been made between labile and stable metal species by using Chelex 100 chelating ion-exchange resin Significant differences in heavy metal speciation were found between an untreated soil and the same soil treated with 100 ppm Zn(II) and 100 ppm Zn(II)–EDTA ions Such a knowledge of speciation may be important with regard to plant availability and uptake

The soluble forms of copper and manganese in effluents from an activated sludge simulation treating a synthetic sewage have been studied[239] Gel permeation chromatography of the synthetic sewage and final effluents indicated that both metals were maintained in solution by organic metal-bonding fractions, although each metal was associated with different fractions The activated sludge simulation was operated with sludge ages from 6 to 18 days Copper speciation in the effluent changed with increasing sludge age where as forms of manganese were little changed The technique used was Sephadex G-15 column phase and flameless atomic absorption The data indicated that association of copper and manganese with different metal bonding components maybe related to the differences in their observed removal efficiencies A review on the fractionation, characterisation and speciation of heavy metals in sewage sludges and sludge amended soils has just been published[240] While the implications for hydrochemical surveys of the organic complexation of Co, Cu and Ni in surface waters has been reported[241]

The gel permeation chromatographic studies by Alloway and his colleagues[242,243] has highlighted the use of exclusion and reversed-phase chromatography for studies of metal speciation (in these cases cadmium and lead) in solutions of heavily polluted soils Thus samples of solutions from soils contaminated with

lead as a result of three different processes, natural weathering and dispersion from an ore body, mining and smelting and sewage sludge amendment to land were fractionated on Sephadex gels Association of lead with organic matter was observed to be higher in soil solutions with an elevated initial pH and this maybe related to the increased stability constants for organolead complexes at higher pH

7 SUMMARY

The reviewer (a second generation chromatographer) has attempted to highlight the various strands and applications of inorganic chromatography These applications now progress beyond the bounds of elemental analysis as probably envisaged by the initiators and pioneers in the field, but personally I feel that the second and third waves of chromatographers (within the inorganic area) have not had the inspiration and foresight of the pioneers —we were seduced by machinery The heart of the separation is still that elusive trinity of interaction between solute, substrate and solvent, it is something that the present generation of chromatographers particularly in the column liquid area has and is realising But many of the breakthrough papers for example in speciation are coming not from "classical" approaches but from other fields where research workers need inorganic chromatography to solve a particular problem To the reviewer the field is a fascinating one, one which is still full of interest and intrigue and that is due in no small measure to the man's birthday we are celebrating, long may it remain so In some areas inorganic chromatography has failed but after some forty years it still progresses— may its middle-age be a fruitful and exciting one I look forward to the next ten years with eager anticipation

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