ELSEVIER

Journal of Chromatography A, 703 (1995) 393–416

JOURNAL OF CHROMATOGRAPHY A

Review

Element-specific chromatographic detection by atomic absorption, plasma atomic emission and plasma mass spectrometry

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Abstract

Reviewed are the principles and applications of contemporary methods of element selective chromatographic detection utilizing atomic absorption, emission and mass spectrometry, these adding an information based dimension to time-based monitoring. Flame and furnace atomic absorption are considered for GC and HPLC detection, while microwave induced plasma (MIP) emission is the focus for GC and inductively coupled plasma (ICP) emission for HPLC. Other plasma emission systems are also reviewed. Both MIP and ICP coupled mass spectrometry are covered for GC and HPLC detection. Supercritical fluid chromatographic (SFC) and field flow fractionation (FFF) interfaces are also considered. Analytical performance in terms of quantitative detection limits and elemental selectivity are considered. Examples are drawn from metal and non-metal detection, considering environmental, petrochemical, geochemical, agricultural and chemical fields.

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0021-9673/95/$09.50
SSDI 0021-9673(95)00281-2

1. Introduction

Central to chromatographic instrumentation is a detection device for qualitative and quantitative determination of the components resolved by the column; this device should respond immediately and predictably to the presence of solute in the mobile phase. Solute property detectors respond to and monitor a physico-chemical property of the eluates directly, providing both a time-based detection dimension and also an information-based dimension such as wavelength of response in electromagnetic spectral detectors.

Spectral property detectors may be structure- or functionality-selective, such as in the mass spectrometer employed in its molecular mode, and the infrared spectrophotometer, and element-selective as for the atomic emission spectrometer or the mass spectrometer, in its elemental mode. The major objectives of the elemental-mode of chromatographic detection are to obtain qualitative and quantitative determination of eluates, often in interfering background matrices, in terms of their elemental constitution. Simultaneous multi-element detection can enable determination of empirical formulae of eluates. In addition to atomic emission element-selective detection, in gas chromatography a number of established element-selective detectors include the nitrogen–phosphorus detector, the flame photometric detector, selective for sulfur and phosphorus, and the Hall electrolytic conductivity detector, which is selective for halogen, nitrogen and sulfur.

The multi-dimensional nature is again evident from the different perspectives for an instrumental device which interfaces the chromatograph with a complex sample characterization device such as the atomic emission spectrometer. For the chromatographer, the spectrometer is a sophisticated chromatographic detector, while for the spectroscopist the chromatograph is a component-resolving sample introduction device.

The renaissance of analytical atomic emission spectroscopy, notably using plasma excitation sources, has re-focused the efforts of chromatographers to employ its capacity in on-line detection [1]. Further, the realization that the ion source employed in plasma atomic emission spectroscopy can be used alternatively as a mass spectral source giving improved chromatographic detectability, has even further extended analytical separation capabilities and sophistication.

From the perspective of sample introduction to the spectroscopic system, analytical chromatography can be classified most usefully in terms of the mobile phase employed. Thus GC, LC and SFC demand different interface designs for effective analyte transfer, whichever spectral detection device is employed. Certain combinations of spectral excitation source and chromatographic mode have proved most useful and these are considered in this review.

There are various capabilities of plasma emission and mass spectral detection which make it a valuable tool for elemental speciation in a wide variety of samples, notably those with complex matrices, such as environmental, petrochemical or biological materials. Interferences from unresolved peaks, which may be present at much greater levels than the targeted analyte, sometimes make it impossible to quantify or even to identify the eluate if a universal detector is used. Element-selective atomic plasma detection can reduce or even eliminate such interferences.

Most valuable is the ability to detect the target element signal without interference or contribution from signals of other elements present simultaneously in the plasma. Selectivity depends on emission spectral or mass spectral properties of the element and of possible inter-

ferences, and on the resolution and other characteristics of the spectroscopic measurement system. A useful measure of inter-element selectivity, at the measured emission wavelength, defines it as the peak area response per mole of analyte element divided by the peak area response of the background element per mole of that element. For the chromatographer, selectivity against carbon is critical, but other elemental background matrices are also important. Selectivities vary greatly among elements, between plasmas and with instrumental conditions, so calibration is necessary. Carbon-selective detection may be considered as a universal detection for organic compounds, analogous to flame ionization, but is more completely independent of carbon atom environment.

The sensitivity for an element in atomic absorption and atomic emission detection depends on the spectral intensity at the measured wavelength, and both sensitivity and selectivity must be considered in the choice of optimal wavelength. Sensitivity, defined by the slope of the response curve, is less often used in atomic spectral than detection limit, expressed as absolute values of element mass (in a resolved peak) or in mass flow-rate units.

Linear dynamic ranges of response in capillary gas chromatography–atomic emission detection (GC–AED) typically extend from the upper linear analyte-carrying capacity of the columns, around 100 ng, to the detection limit of the target element (1–100 pg). In HPLC–AED, the upper limit may be higher since more sample can be accommodated, but the lower limit may also be poorer because of incomplete quantitative transfer of analyte peaks to the plasma. In interfaced chromatography–plasma mass spectrometry, similar or even wider linear ranges are found with typically better detection limits than in chromatography–atomic emission spectroscopy.

Among the attractive possibilities for multichannel GC–AED and also potentially for plasma mass spectral detection is quantitative element ratioing to give empirical formulae of eluates. Measurements are made directly on eluent peaks at sample levels up to six orders of magnitude below those of the classical methods, although precision and accuracy have not matched them as yet.

Various modes of atomic spectroscopy have been interfaced for chromatographic detection, flame emission, atomic fluorescence, atomic absorption, and atomic plasma emission [2,3]. The latter two have been by far the most widely adopted techniques. Chau [4] has reviewed general chromatographic techniques used in metal speciation.

2. Atomic absorption spectroscopic (AAS) detection

Atomic absorption detection for GC was first demonstrated in 1966 by direct introduction of eluent into an unmodified air–acetylene flame [5]. Since that time there have been numerous reports of direct or indirect eluate introduction into flame and furnace AAS [6]. Problems with the simplest approach are excessive condensation of volatilized species in unheated nebulizers, and appreciable dilution by mixing in the burner chamber. Later developments have bypassed nebulizer and burner assembly with direct eluate passage to the atom cell for quartz or graphite furnaces. Chau et al. [7] reported applications of electrothermally heated silica furnace cells for lead and tin organometallics, with thousand-fold sensitivity enhancement over flame AAS. Graphite furnace interfacing for GC was described by Parris at al. [8] with detection limits of 5,7 and 12 ng for methylated arsenic, selenium and tin compounds. GC–graphite furnace AAS (GF–AAS) has been applied for determination of butyltin compounds in sewage utilizing extractions as tropolone complexes and Grignard ethylation [9]. Fig. 1 shows a GC–AAS chromatogram of tin derivatives with 2 ng each of the metal present.

Hydride generation has been explored for alkyltin derivatization from aqueous solutions for both HPLC and GC–graphite furnace AAS [10]. Lobinski et al. [11] developed a comprehensive GC–AED method for tin in water and sediments using diethyldithiocarbamate extraction and

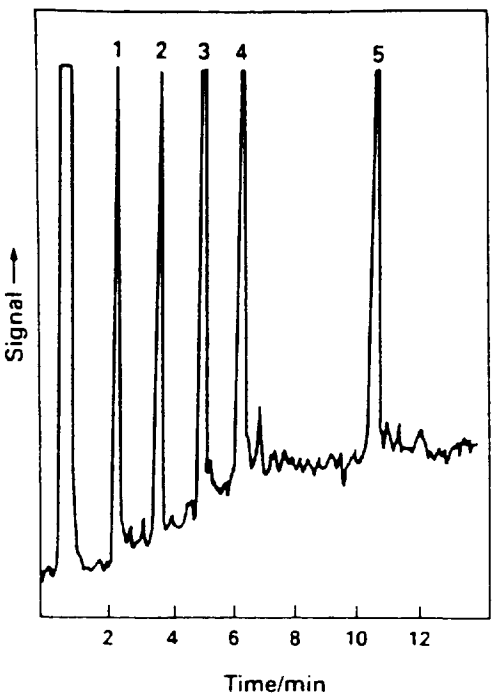

Fig. 1. GC–AAS chromatogram of ethyl derivatives of Sn(IV) and butyltin species. Peaks: 1 = $SnEt_4$; 2 = $BuSnEt_3$; 3 = Bu_2SnEt_2; 4 = Bu_3SnEt; 5 = Oct_2SnEt_2. Each peak represents approx. 2 ng as Sn.

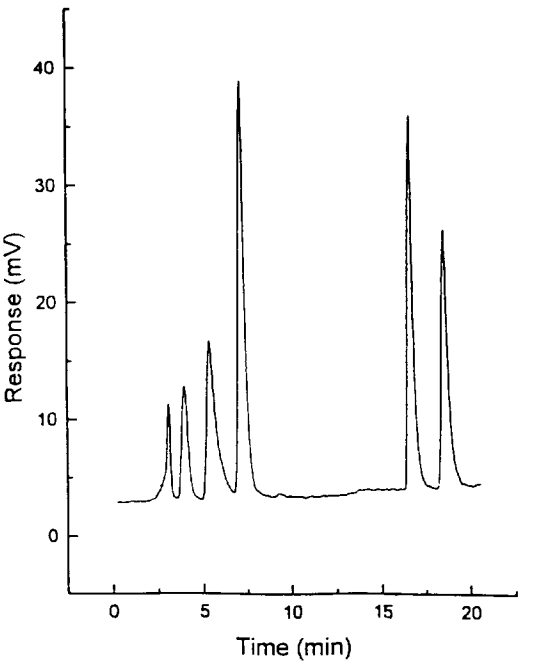

Fig. 2. Gradient elution HPLC–AAS of a 50-μl injection of the 10-ml final extract from lyophilized dogfish muscle (DORM-1), spiked with 5 μg each of arsenate (t_r, 3.06), methyl arsonate (t_r, 3.96), dimethyl arsinate (t_r, 5.37), and arsenobetaine (t_r, 7.04), and 12.5 μg each of arsenocholine (t_r, 16.38) and tetramethylarsonium ion (t_r, 18.27).

Grignard derivatization. They compared quantitation of mono-, di- and tributyl tin with that obtained by GC–AAS obtaining good agreement at the 10–30 ng/ml levels in river water. They also compared a range of hyphenated techniques for tin speciation, including GC–flame photometric detection, hydride generation–GC–GFAAS, GC–MS etc., noting detection limits of ca. 10 pg for GC–AAS.

Interfaced HPLC–GFAAS has been carried out with an automated carousel sampler [12] and a comprehensive comparison between HPLC–AAS and HPLC–ICP–MS has been reported by Hansen et al. [13], who separated seven molecular arsenic forms by anion- and cation-exchange chromatography.

Momplaisir et al. [14] described on-line HPLC–AAS with polar mobile phases by combustion in an oxygen–hydrogen atmosphere in a heated pyrolysis chamber and silica T-tube interface. Products were entrained into an unheated optical tube by the expanding gases, the interface providing equivalent responses to different analyte/element oxidation states to give subnanogram detection for arsenic and selenium anions and cations. Fig. 2 shows gradient elution of a 50-μl injection of lyophilized dogfish muscle, spiked with arsenic species.

3. Atomic plasma emission spectroscopic detection

In contrast with atomic absorption, atomic plasma emission spectroscopy allows simultaneous multi-element measurement, while maintaining a wide dynamic measurement range and good sensitivities and selectivities over background elements. The major plasma emission sources which have been used for gas chromato-

graphic detection have been the microwave-induced helium plasma, operated at atmospheric or reduced pressure (MIP), and the DC argon plasma (DCP). The inductively-coupled argon plasma (ICP) has been little used for GC, but this and the DCP have been used effectively as HPLC detectors. MIP and particularly ICP have been extensively developed as mass-spectral ion sources.

Multidimensional interfaced chromatography–atomic plasma emission spectroscopy permits monitoring for elemental composition with high elemental sensitivity and for specific molecular functionality by derivative element tagging. The specificity of plasma emission enables incomplete chromatographic resolution from complex matrices to be overcome and allows for simultaneous multi-element detection for empirical and molecular formula determination.

3.1. Classes of atomic plasma emission chromatographic detectors

An emission spectral excitation source transforms a sample from a solid, liquid or gas into an energetic plasma of electrons, atoms, ions and radicals in different excited states. Upon deactivation, excited states generate light quanta which produce an elemental emission spectrum. The major types of plasma used in chromatographic detection are summarized here.

3.1.1. Microwave-induced electrical discharge plasma

The principal atom reservoir plasma excitation system used for gas chromatographic detection is the microwave-induced electrical discharge. An argon or helium plasma is sustained in a microwave cavity which serves to focus or couple power from a microwave source into a capillary discharge cell. Microwave plasmas may be operated at atmospheric or reduced pressure depending upon the cavity design [15,16]. Power levels for analytical microwave plasmas are usually low (ca. 50–100 W) making for ease of operation. Their small size permits high power densities however and high electron temperatures are available, notably in the helium plasmas, giving intense spectral emission for many elements, including non-metals. MIP systems have proved less useful for liquid introduction since there is usually insufficient plasma enthalpy to desolvate and vaporize aerosols fully. MIP efficiency depends on the discharge cavities and wave guides used. The latter are metal tubes which transfer power from a microwave generator to the plasma support gas. An interruption in the tube causes total reflection of energy traveling along it, setting up standing waves and forming a resonant cavity. Microwave cavities were compared by Risby and Talmi in their general review of GC–MIP [17]. The most widely used cavity for reduced-pressure helium or argon plasmas has been the 3/4 wave cavity described by Fehsenfeld et al. [18], but the cavities which have been most widely developed for GC–MIP are based upon modifications of the TM_{010} cylindrical resonance cavity developed by Beenakker [19] (Fig. 3).

An advantage of this design is that emitted light is viewed axially, and not transversely through the cavity walls whose properties change with time. The instrumental advantages of atmospheric-pressure operation greatly simplify GC detection. Another type of atmospheric–pressure microwave plasma cavity which has been used successfully in GC–MIP is the "Surfatron" which operates by surface microwave propagation along a plasma column [20]. The plasma may be viewed axially or transversely

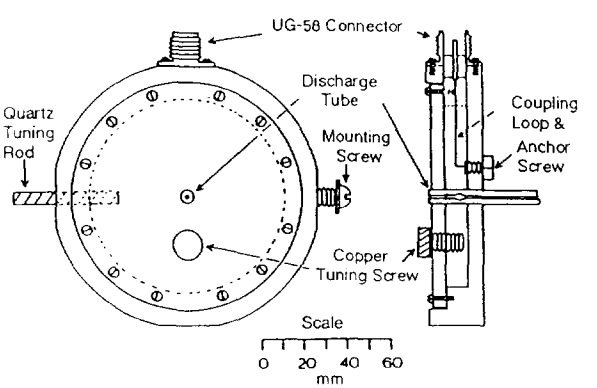

Fig. 3. TM_{010} microwave plasma cavity, based upon the "Beenakker" cavity.

since it extends outside of the plasma structure. This cavity can sustain a discharge over a wide pressure range.

The atmospheric-pressure cavities are very simple to interface with capillary GC columns since the latter can be brought to a few millimeters from the plasma, giving minimal dead volume.

Heating is needed to prevent analyte condensation along the interface. Helium make-up gas or other reactant gases can be introduced within the transfer line to optimize plasma performance and minimize peak broadening. Improvement in the performance of the GC–MIP has been obtained with a threaded tangential flow torch [21], to give a self-centering plasma which can give enhanced emission and better stability. The plasma loses relatively little energy to the walls, thus atom formation and excitation appear to be enhanced by comparison with the straight capillary torch. A disadvantage however is the high volume (l/min) of helium flow gas required.

Specific multi-element monitoring can be accomplished in a variety of ways, a successful method being by a direct reading polychromator displaying up to 12 monitoring wavelengths simultaneously [16,22] with either reduced-pressure or atmospheric-pressure MIP detection. Diode-array detection has shown considerable versatility and sensitivity in a commercial instrument [23] which incorporates an atmospheric-pressure helium MIP with a water-cooled reentrant cavity and discharge tube to maximize signal-to-background signals, and a moveable photodiode-array detector measuring from 170 to 780 nm. Simultaneous detection of up to four elements and display of element-specific chromatograms is possible. The array range is approximately 25 nm, which determines which combinations of elements can be measured in a single experiment. Some analytical figures of merit of this instrument are included in Table 1 which shows elemental detection limits, selectivities and linear dynamic ranges for atmospheric-pressure microwave-induced helium plasma GC detectors.

3.1.2. Inductively coupled plasma (ICP) discharge

The ICP [24] is the most widely used analytical emission spectrochemical source. The discharge is produced by a radiofrequency (RF) field, usually at 27 or 41 MHz, interacting with argon or other gases, flowing through a quartz tube within a copper coil. The RF generator creates a varying magnetic field which in turn generates a circulating eddy current in the heated gas. A stable, spectrally intense plasma discharge is produced with temperatures up to more than 9000 K. Liquid sample introduction involves a spray chamber–nebulizer to generate an aerosol which is carried by the gas into the plasma where solvent is evaporated and the analyte atomized. All compounds should be completely atomized and chemical and molecular interferences are considered to be negligible.

The ICP is compatible with liquid chromatography, since it normally accepts a liquid inlet stream, and HPLC–ICP procedures have been quite widely adopted. It has gained less prominence as a GC detector but may be useful for those elements, mainly metals, whose sensitivity is high in the argon plasma discharge. The rapidly developing field of ICP–MS is gaining wide acceptance and is discussed later with respect to chromatographic interfacing.

3.1.3. Other plasma discharges used in chromatographic detection

The direct-current plasma (DCP) is an electrical discharge maintained by a continuous DC arc and stabilized by flowing inert gas [25]. For chromatographic interfacing, a cathode jet is placed above two symmetrically placed anode jets in an inverted Y configuration [26]. Flowing gas causes vortices around the anodes and a thermal pinch gives an arc column of high current density and temperature. Typical operation is between 500 and 700 W, at 40–50 V. Solutions are introduced from a nebulizer–spray chamber, or vapor-phase samples are directly channeled into the junction of the two columns, and analyte spectral emission is observed from the exhaust plume of the discharge, which consti-

Table 1
GC detection with helium microwave induced plasmas (MIP)

Element	Wavelength (nm)	Detection limit [pg/s (pg)]	Selectivity vs. C	LDR
Carbon (a)	247.9	2.7 (12)	1	>1000
Carbon (b)	193.1	2.6	1	21 000
Hydrogen (a)	656.3	7.5 (22)	160	500
Hydrogen (b)	486.1	2.2	variable	6000
Deuterium (a)	656.1	7.4 (20)	194	500
Boron (a)	249.8	3.6 (27)	9300	500
Chlorine (b)	479.5	39	25 000	20 000
Bromine (b)	470.5	10	11 400	>1000
Fluorine (b)	685.6	40	30 000	2000
Sulfur (b)	180.7	1.7	150 000	20 000
Phosphorus (b)	177.5	1	5000	1000
Silicon (b)	251.6	7.0	90 000	40 000
Oxygen (b)	777.2	75	25 000	4000
Nitrogen (b)	174.2	7.0	6000	43 000
Aluminum (b)	396.2	5.0	>10 000	>1000
Antimony	217.6	5.0	19 000	>1000
Gallium (b)	294.3	ca. 200	>10 000	>500
Germanium (a)	265.1	1.3 (3.9)	7600	>1000
Tin (a)	284.0	1.6 (6.1)	36 000	>1000
Tin (b)	303.1	(0.5)	30 000	>1000
Arsenic (b)	189.0	3.0	47 000	500
Selenium (b)	196.1	4.0	50 000	>1000
Chromium (b)	267.7	7.5	108 000	>1000
Iron (b)	302.1	0.05	3 500 000	>1000
Lead (a)	283.3	0.17 (0.71)	25 000	>1000
Mercury (b)	253.7	0.1	3 000 000	>1000
Vanadium (b)	292.4	4.0	36 000	>1000
Titanium (b)	338.4	1.0	50 000	>1000
Nickel (b)	301.2	1.0	200 000	>1000
Palladium	340.4	5.0	>10 000	>1000
Manganese (b)	257.6	1.6(7.7)	110 000	>1000

Detection limit: 3 times the signal-to-noise ratio. LDR = linear dynamic range. (a) Conventional TM_{010} MIP (University of Massachusetts). (b) Hewlett-Packard 5921A (Hewlett-Packard or University of Massachusetts).

tutes the excitation source. The DCP has been interfaced with both HPLC and GC.

A 60-Hz alternating current helium plasma (ACP) has been employed as a GC detector. It forms a stable, self-sustaining emission source, requiring no external initiation and which does not extinguish under high solvent loads [27]. Simplicity of construction and operation are distinct advantages.

Atmospheric-pressure capacitively coupled plasma (CCP) discharges have been developed as sources for atomic spectroscopy [28,29]. The small volume of this plasma has allowed its use for capillary GC without notable band broadening. It can sustain a stable plasma from 10–500 W at 200 kHz to 30 MHz, and carrier gas flow-rates as low as 20 ml/min [29].

A series of studies on low-frequency, high-voltage electrodeless discharges sustained in argon, nitrogen and helium, suggested good possibility for application of emission from the atmospheric–pressure afterglow in GC detection. The helium system is most favored because the metastable energy carriers have the capa-

bility of the highest collisional energy transfer and thus the best ability to excite other elements to emission [30].

3.2. Chromatographic eluent introduction

Since eluent from GC and HPLC columns is normally at atmospheric pressure, simpler interfacing configurations are possible with atmospheric-pressure plasmas than for reduced-pressure plasmas. The microwave-induced plasmas (MIP) have found much wider use in GC than in HPLC interfacing although the application of the direct-injection nebulizer (DIN) for microbore column effluent flow-rates may expand the latter's potential [31].

3.3. Atomic plasma emission gas chromatographic detection

Gas chromatography has most often been the first choice for chromatographic sample introduction into all types of plasmas and approximately one hundred papers attest to the value of this interface. This area is considered based upon different elements and sample types, and the preferred plasmas for their determination.

3.3.1. Non-metallic hetero-atom compounds

The helium microwave-induced plasmas (MIP) have been the most used for non-metals detection, since for many of these elements, argon metastable energy carriers show insufficient collision energy transfer for adequate excitation. The argon-MIP, DCP and ICP have shown some utility however for elements such as fluorine, phosphorus and silicon.

McCormack et al. [32] and Bache and Lisk [33] first reported practical reduced-pressure argon GC–MIP effective for selective detection of P, S, F, Cl Br, I, and C, with detection limits between 10^{-7} and 10^{-12} g/s, but selectivities against carbon were poor. McLean et al. [16] developed a tunable detection system using scavenger gas to prevent carbon deposits from forming on the inside of the plasma tube. Detection limits were in the 0.03–0.09 ng/s range for C, H, D, F, Cl, Br, I and S. Accurate H/C atomic ratios were also reported for a number of hydrocarbons.

Trivalent arsenic and antimony were determined with detection limits of 20 and 50 pg [34] in environmental samples by reduced-pressure GC–MIP at 228.8 nm and 259.8 nm, respectively, using derivatization and reaction to form triphenylarsine and triphenylstibine. Using the polychromator-based instrument mentioned above [22], Hagen et al. [35] used elemental derivatization with chlorofluoroacetic anhydride to enable Cl and F specific detection of acylated amines. Zeng et al. [36] have focused on improvements in oxygen specific detection with a similar reduced-pressure system. Highly pure plasma gases and careful exclusion of air improved the limit of detection to 0.3 ng/s.

Sklarew et al. [37] noted that while the low-pressure Evenson source provides optimal excitation energy for non-metals, its sensitivity is lower than that of the Beenakker cavity because of its transverse viewing geometry. The atmospheric-pressure Beenakker cavity provides a more efficient way to couple microwave energy into the plasma, and with its axial geometry is more sensitive; however its high pressure causes tube erosion, at least if the discharge tube is not cooled, thus causing reliability problems.

Increased efficiency of transfer of microwave power to the discharge using such cavity structures as the Beenakker TM_{010}, allows plasmas to be sustained at atmospheric pressure at the low power levels possible with reduced-pressure cavities. A further advantage is the ability to view light emitted from the plasma axially.

The first study of the TM_{010} for packed-column GC detection [38] split the GC effluent between a flame-ionization detector and a valve which allowed it to be directed to a vent or to the plasma. As the plasma could not tolerate vapor pulses larger than those corresponding to 0.1 ml of GC analyte (injected solution), venting of solvent was always needed for packed-column work. This is also the main reason why HPLC interfacing with the cavity has been largely unsuccessful.

The first major application of the plasma was to halogen-specific detection of purgeable

haloorganics in drinking water [39]. Although the MIP is less sensitive than the electron-capture detector for polyhalogenated compounds, it typically responds uniformly to the content of each halogen irrespective of analyte molecular structure. Sub-ppb detection and quantitation of trihalomethanes was readily achieved by extraction and "purge and trap" techniques. An advantage over the HECD is the specificity for individual halogens. Polyimide-coated flexible fused-silica capillary columns can be interfaced to within a few mm of the plasma, and such direct interfaces have been widely used in capillary GC–MIP. An alternative gas-switching system, incorporating a deactivated valveless fluidic logic device was effective in transfer of chemically active and thermally sensitive trialkyl lead chlorides at the sub-ng level [40]. A comprehensive evaluation of MIP detection was carried out with this system [41]. Some detection limits and selectivities from this study are listed in Table 1 along with those from other investigations.

A number of developments show the utility of GC–MIP research and applications; widespread adoption of the technique for more routine use is now feasible with the introduction of a commercial instrumental system [23]. Near-infrared atomic emission has been investigated in GC–MIP, a cooled TM_{010} cavity and TFT being used at 370 W with a Fourier transform NIR spectrometer [42]. Computer-generated element specific chromatographic reconstructions for eight non-metals, C, H, N, O, F, Cl, Br and S, were obtained from one injection. Atomic emission intensity was plotted against retention time to coincide with element spectral NIR region. Both the FT approach and the spectral region examined for non-metallic elements suggest a worthwhile extension of GC–MIP application.

Oxygen-selective detection with a linearity of three decades has been reported by Bradley and Carnahan with a TM_{010} cavity in a polychromator system [43]. Background oxygen spectral emission from plasma gas impurities, leaks or back-diffusion into the plasma were minimized to give sensitivities between 2 and 500 ppm in different complex petroleum distillates. The selective detection of phenols in a light coal liquid distillate is shown in Fig. 4.

Andersson and Schmid [44] used GC–MIP–AED in trace analysis for C, S, Cl, Br, O in coal tar, obtaining good detection for dibenzodioxin

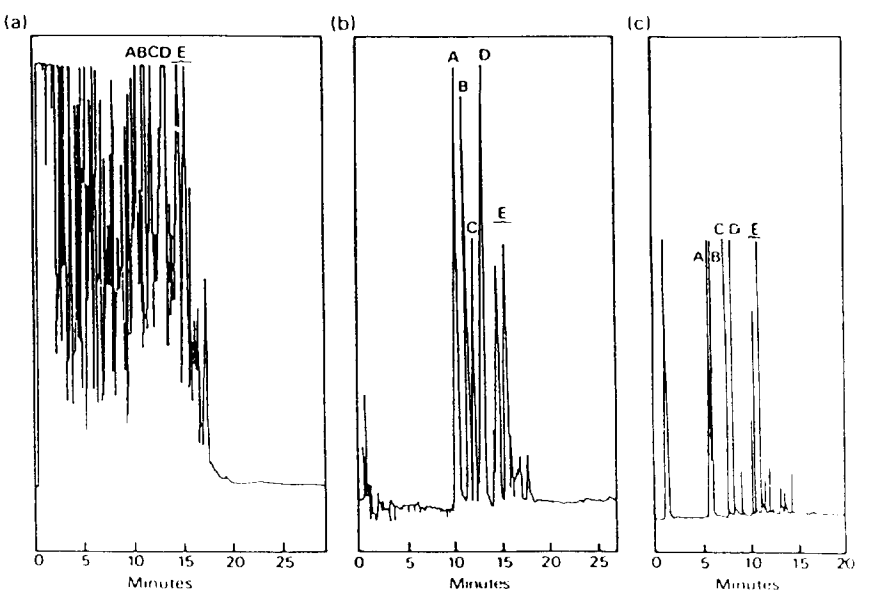

Fig. 4. GC–AED of light coal distillate: (a) carbon MIP; (b) oxygen MIP; (c) FID trace of phenolics concentrate of the same distillate. Peaks: phenol (A), *o*-chlorophenol (B), *o*-cresol (C), *m*- and *p*-cresols (D), C_2-phenols (E).

and dibenzofurans. They also examined dual isotope detection for ^{12}C and ^{13}C in consideration of the utility of the latter tagged compounds as internal standards; this isotopic resolution uses the observed spectral selectivity of 2500 obtained between ^{12}C and ^{13}C molecular emission bands. Fig. 5 shows sulfur-selective detection of a coal tar extract with an without subtraction of carbon background emission.

Kosman [46] has developed valuable applications of GC–AED using the diode-array detection system, to a range of petroleum-related problems. In a study of simulated distillation (SIMDIST) monitoring, he described multi-element information of petroleum mixtures as a function of boiling point, for C, H and S. Also obtained were H/C molar ratios and CHS elemental formulae for each 1% carbon evolved [45]. He also reported on pattern recognition to examine SIMDIST profiles, measured low-molecular-mass sulfur gases and monitored levels of C, H, D, S, N, O and Cl in multi-element analyses [46]. Sandra [47] also reports GC–AED of species such as carbonyl sulfide in air pollution monitoring studies.

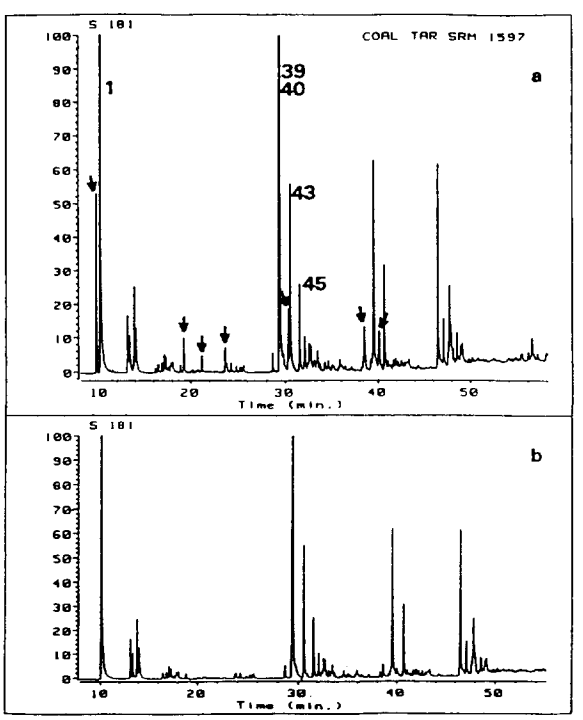

Fig. 5. Sulfur specific GC–AED of coal tar standard extract SRM 1597 (benzo and naphtho-thiophenes), (a) without subtraction of carbon emission, (b) with subtraction of carbon emission.

In the characterization of fossil fuel and petroleum precursors, pyrolysis GC–AED has been successfully applied for kerogens [48]. On-line pyrolysis of mg amounts of ground solid samples has given valuable information on the sulfur and nitrogen profiles of pyrolyzate products. Of particular interest was the observation in Fig. 6 of trace level organoarsenic compounds produced over a wide boiling point range. In this kerogen pyrolysis, an on-line butylation process using tributylammonium hydroxide also showed clearly the presence of organoselenium compounds.

An important development of GC–AED which promises considerable application to the study of aroma volatiles and air quality is the use of interfaced dynamic head-space analysis for GC sample introduction. Head-space gas chromatography (HS-GC) reduces or eliminates sample preparation, and it is thus useful to minimize chemical changes in volatile flavor and aroma components during the analytical procedure. It can increase detection sensitivity by two or three orders of magnitude over conventional sampling methods. HS-GC–AED has been used to detect and identify trace levels of volatile organoselenium from garlic. Selenium has received much attention in the last decade arising from the recognition of its essential nutritional role and from reports of selenium toxicity in humans.

Simultaneous element-selective gas chromatograms of volatile species evolved from elephant garlic are shown in Fig. 7 [49]. Empirical formula calculation utilizing compound-independent calibration [50] together with GC–MS was used for qualitative identification of the selenium containing peaks.

Brill et al. [51] evaluated fluorine-selective monitoring at 685.6 nm obtaining a 4.8 pg F/s detection limit. Application to organofluorine compounds in a fluorinated substrate administered to a mixture of wheat germ phosphatase and potato apyrase was described [51]. The

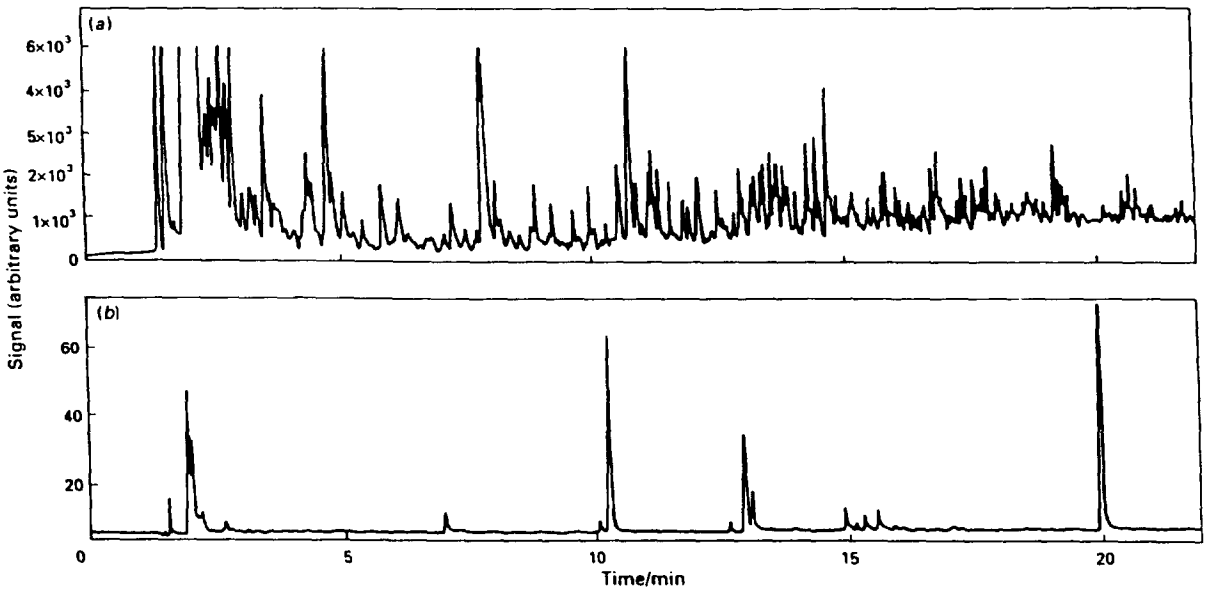

Fig. 6. Carbon specific, 193 nm (a) and arsenic specific, 189 nm (b) pyrolysis GC of Monterey kerogen pyrolyzed at 800°C for 10 s.

diode-array GC–AED system has been evaluated for the simultaneous detection of fluorine- and oxygen-containing molecules. Hydrogen and methane gases were used to produce a carbon coating on an alumina plasma discharge tube thereby reducing etching by fluorine in the plasma. This significantly reduced spurious oxygen signals and gave a high degree of response selectivity against fluorinated species containing no oxygen [52].

Much attention has been paid to the question of compound-independent calibration of AES responses, i.e. the independence of elemental molar response ratios as applied to the calculation of empirical formulae. Huang et al. [53] concluded that elemental responses for C, H and Cl were affected by molecular structure. Valente and Uden concluded analyte level dependencies existed for response factors [54]. Kovavic and Ramus [55] have carried out an extensive study for the diode-array detector of the validity of compound-independent calibration (CIC) for C, Cl, F, N, O. Relative standard deviations of elemental response factors were found to be between 3 and 6% for a wide range of compounds [55]. Webster and Cooke have noted that for oxygen detection, the slopes of the graphs of concentration vs. elemental response vary with molecular structure and also with the condition of the discharge tube [56].

Pedersen-Bjergaard et al. [57] studied molecular formulae for halogenated alkybenzenes and pesticides and concluded that the inclusion of complementary data from other techniques such as GC–MS gave the most secure assignments.

An example of multi-element detection with the diode-array detection system is shown in Fig. 8, chlorine, fluorine and phosphorus detection being obtained in a chromatogram of a green onion extract fortified with a number of pesticides at the sub-ppm level [58].

The Surfatron-MIP has proved to be of value in determination of P, S, Cl and Br in pesticides, with detection limits ranging from 3 to 60 pg/s [20]. This study also compared results obtained over a pressure range from 20 to 760 Torr, concluding that best results were obtained at 50 Torr.

A stabilized capacitive plasma (SCP) has shown long term stability and minimal matrix interferences; the plasma tube is mounted directly to the end of the capillary column and emitted

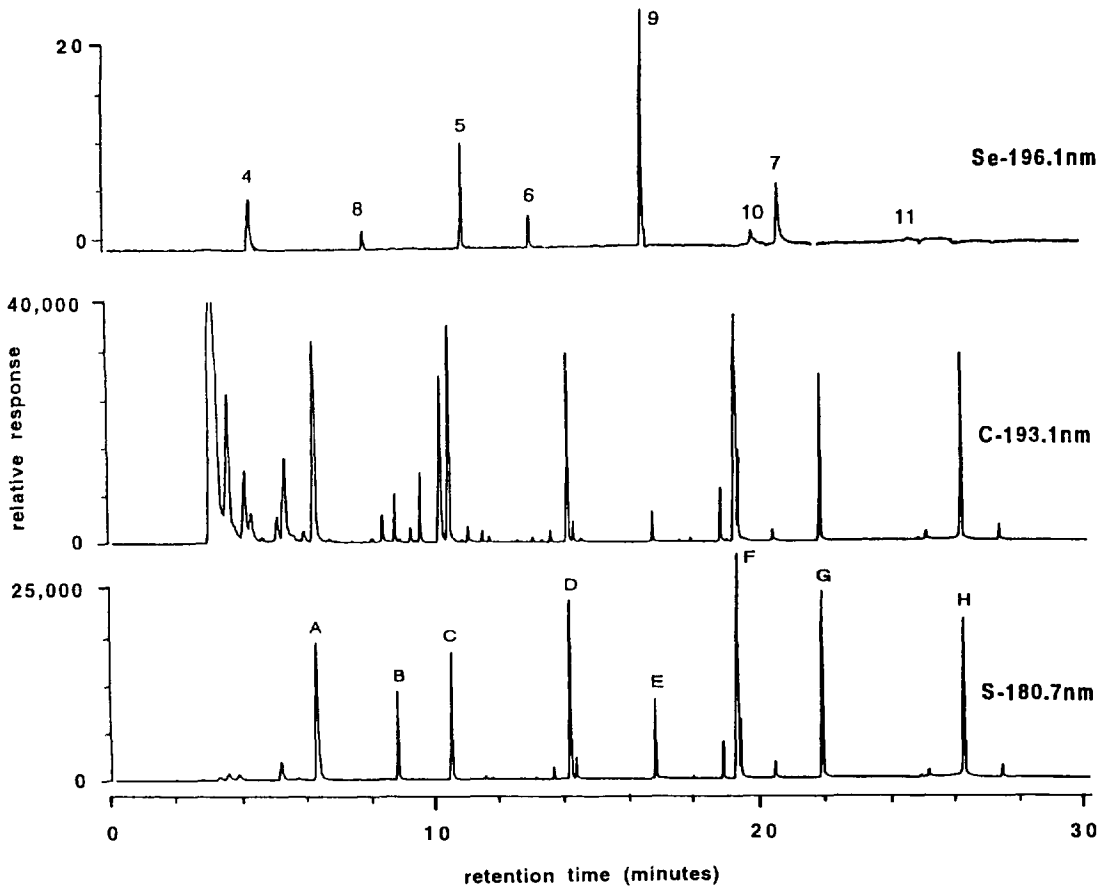

Fig. 7. Simultaneous detection of carbon, sulfur and selenium compounds in elephant garlic detected by head-space-GC–AED. Selenium compounds: 4 = dimethyl selenide (MeSeMe), 5 = methanesulfenoselenoic acid methyl ester (MeSeSMe), 6 = dimethyl diselenide (MeSeSeMe), 7 = bis(methylthio)selenide [$(MeS)_2Se$], 8 = allyl methyl selenide (MeSeAll), 9 = 2-propenesulfenoselenoic acid methyl ester (MeSeSAll), 10 = 1-propenesulfenoselenoic acid methyl ester (MeSeSCH = CHMe), 11 = (allylthio)(methylthio)selenide (MeSSeSAll). Sulfur compounds: A = MeSAll; B = MeSSMe; C = AllSAll; D = MeSSAll; E = MeSSSMe; F = AllSSAll; G = MeSSSAll; H = AllSSSAll.

light is transferred through a glass fiber optic to a polychromator measuring non-metal emission in the 650–1000 nm range [59].

The argon DCP system has been used to detect non-metal elements such as boron and silicon present in GC derivatizing groups. For silicon, the absence of interfering spectral response from the quartz discharge tube often used in the MIP is an added advantage, a selectivity of silicon over carbon of $2 \cdot 10^6$ with a detection limit of 25 pg/s being reported [60]. The 3 pg/s detection limit reported for boron was similar to that obtained in the MIP.

Despite its popularity as a spectroanalytical emission source, the ICP has received little attention as a GC detector, however, it does have the advantage of withstanding organic solvents better than the MIP because of its higher plasma temperature. In the first evaluation of GC–ICP performance, a packed column was

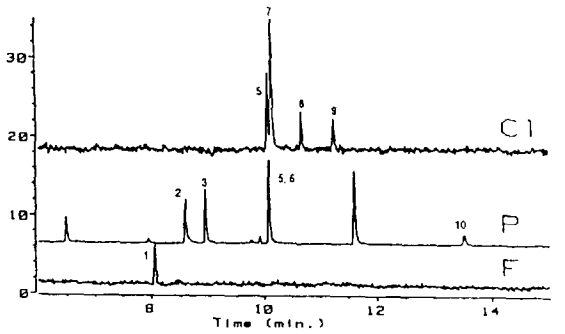

Fig. 8. GC–AED of chlorine, fluorine and phosphorus compounds from green onion extract fortified with pesticides. Peaks: 1 = ethalfluralin, 2 = dimethoate, 3 = diazinon, 4 = chlorthalonil, 5 = chlorpyrifos, 6 = parathion, 7 = dimethylchlorthal, 8 = folpet, 9 = dieldrin, 10 = methylazinphos.

interfaced to a demountable ICP torch through a "T" which enabled make-up argon to be added [61].

3.3.2. Metallic hetero-atom compounds

While detection limits and selectivities for metals are usually better than for non-metals, because of emission intensity and absence of background in the spectral region monitored, GC applications for metallic compounds are less common than for non-metals. The principal difficulties involve gas chromatographic stabilities at the column temperatures needed for GC. However, many volatile organometallic and metal–chelate compounds can be quantitatively gas chromatographed [62], and GC–AED detection methods are most valuable in confirming elution of inorganic species of previously unconfirmed vapor-phase stability, and acquiring sensitive analytical data.

Table 1 shows GC–MIP data for many transition and main group metals, some of them, notably lead, and mercury having been the subject of a number of studies. Each of these elements is determinable by GC–MIP with TM_{010} cavities to sub-pg/s detection limits. An early example of an environmental analysis was of lead and carbon specific detection for trialkyllead chlorides extracted from an industrial plant effluent and derivatized with butyl Grignard reagent to form their analogous trialkylbutyllead compounds [40]. The degree of chromatographic interference from the high level of carbon-containing compounds prevented any qualitative or quantitative determination of the trialkyllead compounds by GC–ECD or GC–MS without extensive clean-up and loss of analyte.

In a study comparing reduced- and atmospheric-pressure MIP systems, Olsen et al. found a 1-pg detection limit for mercury for the latter system, with selectivity over carbon of 10 000 [63].

The diode-array detection system now in wide use has been applied for comprehensive ultratrace speciation of organo-tin and -lead compounds in sediments and aqueous environmental samples [64]. Lobinski and Adams measured sub-ng/ml organolead speciation by concentration in Tenax packed liner [65], Fig. 9 showing a series of chromatograms for lead determination.

Lobinski et al. [11] developed a comprehensive GC–AED method for tin in water and sediments, the absolute detection limit being ca. 0.05 pg as Sn, using diethyldithiocarbamate extraction and Grignard derivatization, making comparisons with GC–AAS.

Metal chelates with sufficient volatility and thermal stability for gas chromatography have received much attention over the past 20 years, with most emphasis being placed on complexing ligands of 2,4-pentanedione (acetylacetone) and its analogs; this area has been comprehensively reviewed recently [62]. Among examples of application have been GC–MIP analysis for chromium as its trifluoracetylacetonate in blood plasma, with excellent quantitation and precision [66]. Trace determinations of beryllium, copper and aluminum have also been reported and ligand redistribution and reaction kinetics of gallium, indium and aluminum chelates have been followed by MIP detection [67].

Fig. 10 illustrates the application of the reentrant cavity/diode-array system for specific detection of copper, nickel and palladium chelates

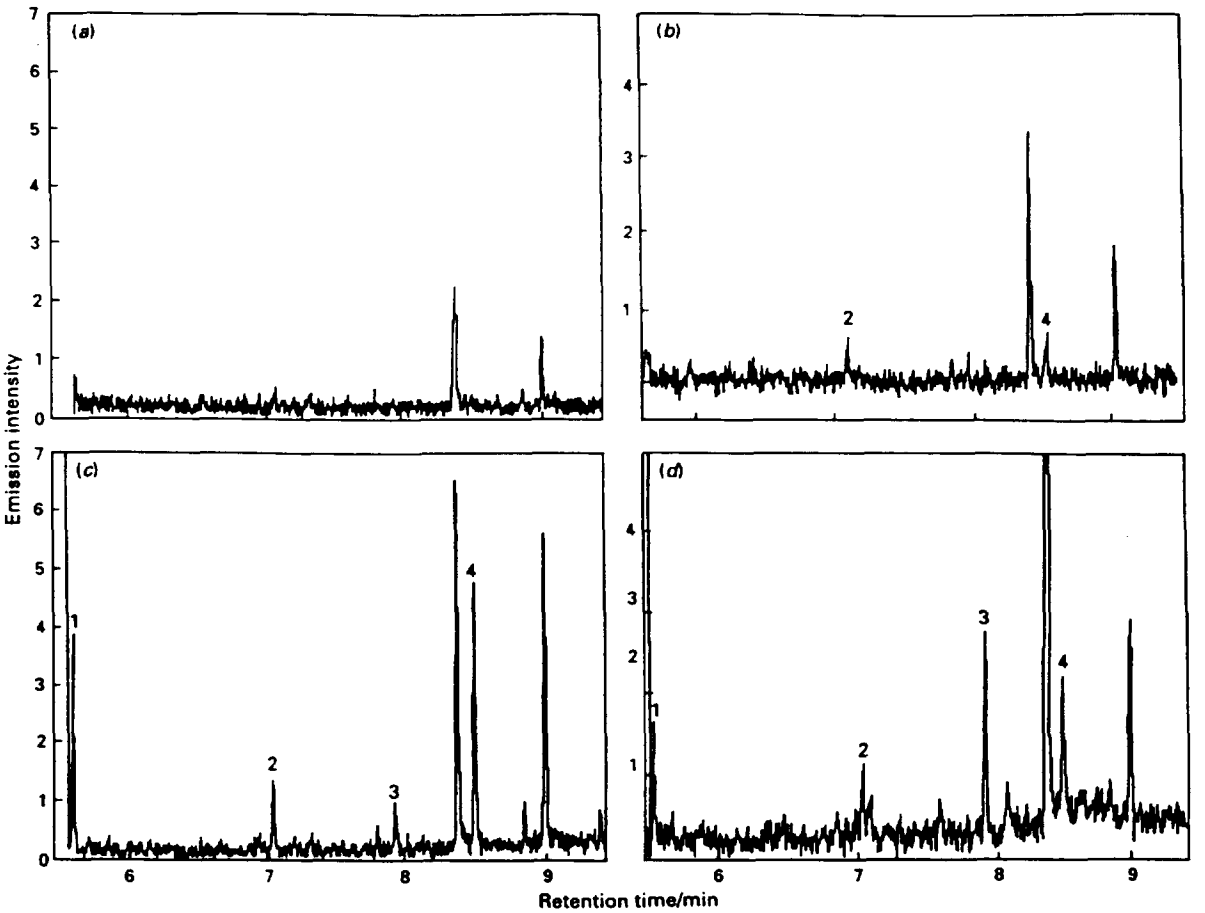

Fig. 9. Lead-specific GC–AED of propylated organolead species. (a) Blank during derivatization of pure hexane with propylmagnesium bromide; (b) blank from complete analytical procedure; (c) chromatogram of tap water; (d) chromatogram of a polar snow sample. Peaks: 1 = Me_3Pb^+; 2 = Me_2Pb^{2+}; 3 = Et_3Pb^+; 4 = Et_2Pb^{2+}.

of N,N′-ethylene-bis(5,5-dimethyl-4-oxohexane-2-imine) which forms very stable chelates with many divalent transition metals [68].

GC–AED has been applied to the determination of metalloporphyrins in the fingerprinting of crude oils [69,70]. Vanadium, nickel and iron form porphyrin-like structures and have been quantitated by high temperature GC up to 400°C following size-exclusion isolation of crude oil fractions.

Pi-bonded organometallics such as metallocene derivatives have proved well-behaved in capillary GC; a TM_{010} cavity gave excellent detection of iron, cobalt, nickel, chromium, manganese and vanadium compounds, verifying elution of some previously unchromatographed compounds [71].

3.4. Liquid chromatographic applications of AES detection

Most development in plasma spectral detection for HPLC has been with the ICP and to some extent the DCP, in contrast to the dominance of the microwave-induced plasmas as element-selective GC detectors. Metal specific detection is predominant and will probably remain so until better interface systems can be

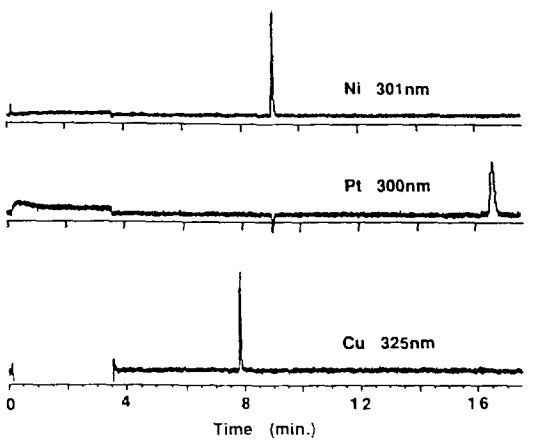

Fig. 10. Copper, nickel and palladium GC–AED of a mixture of chelates of N,N'-ethylenebis(5,5-dimethyl-4-oxohexane-2-imine).

devised to remove HPLC mobile phases while transferring eluate peaks to a plasma optimized for non-metals. This interface may incorporate a moving-band eluate transport device or it may be based on thermospray or particle beam technology.

The major problem in HPLC–plasma interfacing is plasma incompatibility with the typical analytical flow-rates of mobile phases. Specific-element atomic spectroscopic detectors typically employ on-line nebulization and excitation of small volumes (5–200 μl) of liquid, conversion into aerosol and introduction into an atomization–excitation cell. The relatively poor detection limits result from the incomplete conversion of effluent flow into aerosol and its transport; typically only 1–5% of the sample reaches the plasma. Poor tolerance of the plasma is also observed for common solvents used in HPLC, particularly in reversed-phase ion-pairing and size-exclusion chromatography. Solution to these problems lies in more quantitative nebulization, atomization and excitation of HPLC samples as well as in improved transport systems.

3.4.1. HPLC–ICP detection

Many reports of HPLC–ICP have appeared but detection limits for many elements are often barely sufficient or insufficient for elemental speciation in real samples of environmental significance. An early study used "simulated peaks" for detection of copper chelates in aqueous media with a 1.2 kW argon plasma. Detection limits in μg/l were Cu(6.8), Ni(43), Co(21), Zn(19), Cd(89), Cr(20) and Se(280) [72] and subsequent work has seen little general improvement of such results. MDLs are usually two or more orders of magnitude worse than for continuous-flow ICP–AES. Normal-phase HPLC where organic solvents such as hexane or methylisobutylketone are used provide a greater challenge, since ICP behavior is less well defined and spectral background interference is greater. One approach was microbore HPLC, with lower mobile-phase flow-rates and a simple T interface. For test samples of copper and zinc diketonates and dithiocarbamates, peak broadening was minimized by optimal design of the interface to give virtually constant peak-width ratios for ICP and UV detection [73].

HPLC–ICP has been effective for metalloid elements; a 130 ng/ml detection limit for arsenic in organoarsenic acids was found for 100-μl samples [74]. The spectrometer was a simultaneous unit with 48 channels operating at 1.2 kW. A single-wavelength study [75] measured arsenic and cadmium compounds at the As emission wavelength of 228.812 nm, using also the Cd emission line at 228.802 nm. Detection limits were 2.6 ng/s (3.1 ng/ml) for As as arsenite and 0.059 ng/s (0.12 ng/ml) for Cd as the nitrilotriacetate. Gardiner et al. studied copper, iron, zinc and cobalt in human blood, serum, milk and seminal fluid [76] while Mazzucotelli et al. investigated organometallics in a marine ecosystem [77].

Hausler applied size exclusion chromatography (SEC)–ICP for elemental profiling of fuel liquids and oils, determining that simultaneous profiling of the molecular size distribution of sulfur-, vanadium- and nickel compounds in petroleum crudes and residua provides valuable fingerprint identification of oils [78]. Ferritin, an iron-containing protein which exists in a number of discrete forms has been analyzed using aqueous SEC in phosphate–hypochlorite buffers; good repeatability was found for detected iron

levels at the ng level [79]. Mazzucotelli et al. determined trace levels of Cd, Zn and Cu metalloproteins in marine mussels using SEC with sequenced UV absorption detection before the ICP [80].

Dorn and Skelly Frame [81] have obtained detection limits for silicon of 4–5 ng in a study of silanol and polysiloxane chemistry in which they used both size-exclusion chromatography with tetrahydrofuran and xylene as mobile phases, and reversed-phase partitioning with a water–acetonitrile mobile phase [81]. Fig. 11 shows a schematic diagram of the system used which incorporated rapid switching between the normal peristaltic pumped sample introduction and HPLC.

A possible solution to overcome the difficulties in quantitative transfer of HPLC eluate to the ICP involves a total injection microconcentric nebulizer (DIN) which can achieve almost 100% nebulization and transport efficiency [31]. Detection limits ranging from 164 ng/ml for sulfur to 4 ng/ml for zinc have been reported. Approaches to improve the performance of HPLC–ICP include miniaturized plasma torches, water-cooled spray chambers, low-power and low-flow torches, aerosol cooling and oxygen doping.

3.4.2. HPLC–DCP detection

The tolerance of the DC argon plasma to a wide range of solvents has aided its use as an LC detector. The first procedure described for HPLC–DCP used standard nebulization for reversed-phase chromatography, but an impact device was found superior for normal-phase hydrocarbon and halocarbon eluents. Ni, Cu, Hg and Cr chelates were determined with mass flow detection limits of 0.3 ng/s for copper and 1.25 ng/s for chromium [82]. Applications for the inorganic anions sulfate, nitrate and acetate as their cadmium salts were reported, but minimum detectable levels in the 100 ppm range limited applicability [83]. The determination and speciation of Cr(III) and Cr(VI) (as chromate) by reversed-phase ion pairing gave detection in the 5–15 ppb range [84]. Applications included biological samples from ocean floor drillings, chemical dump site, surface-well water and waste water samples. A practical application of DCP detection involved determination of tin levels down to 10 ppb by a combination of HPLC with continuous on-line hydride generation followed by DCP measurement. The method was found to be suitable for analysis of alkyltin chlorides as well as stannous and stannic cations [85]. Urasa

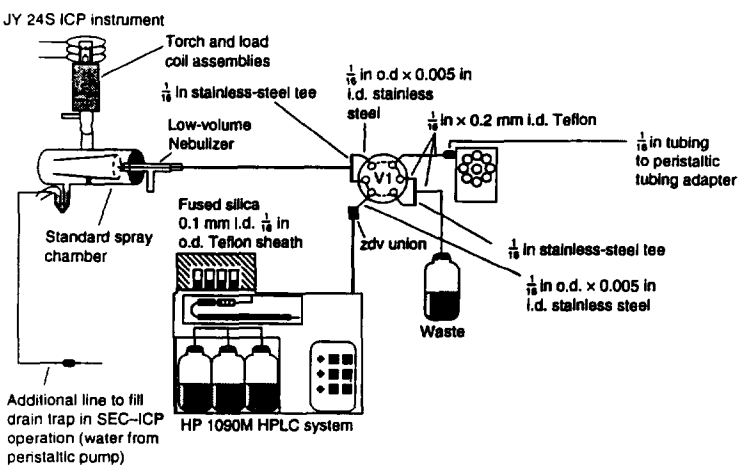

Fig. 11. Schematic diagram of HPLC–ICP system with tubing and valve connections to allow instantaneous switching between normal and HPLC sample introduction.

and Nam [86] used DCP for Cr and V species and attained 1 ppb limits through use of an on-column preconcentration procedure.

The ion-pair chromatographic (IPC) behavior of inorganic mercury(II) and organomercurials was investigated with tetra-*n*-alkylammonium bromides as ion-pair reagents and sodium halides in methanol–water as mobile phases. UV and DCP specific-element detection were employed. The effects of the type and the concentration of sodium halide and ion-pair reagent, and the level of methanol on chromatographic behavior of mercury compounds were evaluated [87].

3.4.3. HPLC–ACP detection

The AC plasma has also been characterized as a HPLC detector by Colon and Barry [88]. Reversed-phase eluent was introduced into the plasma by a frit nebulizer and the plasma could tolerate 100% methanol without extinguishment. The behavior of organomercury compounds was investigated in the ng–μg range and a detection limit of 2.2 ng/s of mercury was obtained for methylmercuric chloride.

3.4.4. HPLC–MIP detection

As has been discussed, HPLC–plasma interfacing has developed most with the high powered DCP and ICP argon plasmas which are able to tolerate mobile phase solvents at the flow-rates used in the different chromatographic procedures. The low powered helium MIP however cannot be directly interfaced to conventional HPLC columns, since the discharge will be quenched by continuously introduced ml/min liquid flow streams. Some approaches to this problem have been explored. The only direct introduction of liquid into an MIP was by flowing the HPLC effluent over a heated wire and vaporizing it by a cross-stream of helium into the discharge. This system shows some potential for reversed-phase separations [89]. A mixed-gas oxygen–argon MIP sustained in a modified discharge tube consisting of two concentric quartz tubes was applied successfully for HPLC of mercury compounds. Methanol–water mixtures with up to 90% of the former solvent were tolerated; detection limits for organically-bound Hg were in the ng range, but response was found to be dependent upon molecular structure [90]. A high-power (kW) discharge, operating in the radiofrequency or microwave range, accommodated continuous solvent-flows provided that nebulization was adequate [91]. The incentive for developing a viable HPLC–helium MIP interface is considerable because of the potential for monitoring of non-metallic elemental effluents; this is difficult or impossible with argon DCP and ICP systems. A moving-wheel sample transport–desolvation system has been described in which aqueous solvent is evaporated with a flow of hot nitrogen, leaving dry analyte which is transported into the plasma, where it is volatilized, atomized and excited. The plasma used was a small-volume helium MIP, operated at 100 W, with helium support gas-flow of 3.1 l/min. Detection limits were in the range 4 ng/s for iodine to 300 ng/s for bromine [92]. The LC–MIP interface is shown in Fig. 12.

Mason et al. utilized a moving band interface to separate solvent from analyte, and a 125 W Beenakker MIP. Spectral scans indicated complete removal of a 80:20 water–methanol mobile phase. Separation on an ODS column for 9-chlorofluorene, *p*-chlorobiphenyl etc. gave detection of a few 100 pg/s [93].

The direct injection nebulizer (DIN) noted earlier [31] may provide one answer and another involves the removal of the solvent perhaps by adaptation of the thermospray and particle-beam approaches now used in HPLC–MS. The interfacing problems for low-power MIPs are comparable to those in HPLC–MS and HPLC–FTIR. Another solution to the problem may be cryofocusing as used in the latter technique. Investigations are also underway on alternative plasma cavities which may be able to sustain the helium MIP under conventional HPLC flow conditions. Capillary HPLC columns with mobile-phase flow-rates of a few ml/min provide an interesting possibility for helium MIP interfacing, but sample capacity may limit application for trace determinations.

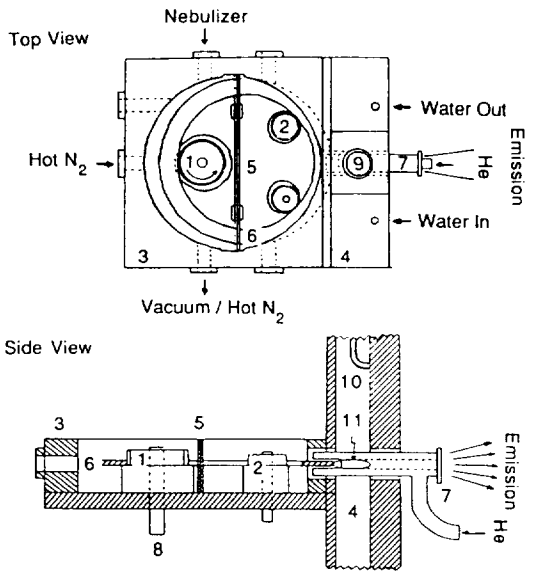

Fig. 12. LC–MIP interface: 1 = friction drive wheel; 2 = guide wheel gearing; 3 = interface chamber housing; 4 = TM_{010} cavity; 5 = separation plate; 6 = stainless steel wheel; 7 = fused-silica plasma torch with fused-silica face plate; 8 = driver wheel shaft; 9 = N connector; 10 = coupling loop; 11 = plasma region.

3.5. Supercritical fluid chromatographic applications of AES detection

Although analytical SFC was demonstrated in the early 1960s, the recent availability of high-resolution packed and capillary SFC columns and instrumentation has led to renewed interest in the technique. High-resolution SFC along with supercritical fluid extraction (SFE), promises to allow separations in areas where neither GC or HPLC may be possible. Adoption of detectors for SFC has proceeded in two main directions; for methodology and instrumentation derived from GC, the flame-ionization detector has been favored, while for development related to HPLC, the UV–Vis spectrophotometric detector has been adopted. Plasma emission is a natural development because of its use in both GC and HPLC. An initial report described an ICP interface with close to 100% atomization efficiency [94].

A Surfatron MIP sustained in helium was employed for SFC detection, giving sulfur-specific detection at 921.3 nm with a 25 pg/s limit for thiophene [95]. Extensive spectral characterization was carried out in this system for two common SFC mobile phases, carbon dioxide and nitrous oxide [96]. Skelton et al. evaluated radiofrequency plasma for S and Cl in the near IR obtaining 50–300 pg/s detection limits [97]. Webster and Carnahan coupled SFC with a 500 W helium MIP for non-metals, near IR being used for Cl and S and UV–Vis detection for C and H. Detection limits of 0.8 ng/s were obtained for S using carbon dioxide with a shot noise limited system [98]. Webster and Carnahan compared 500 W and 60–150 W helium MIP plasmas for packed-column SFC, peak areas remaining unchanged from 150 to 250 atm. [99].

Modification of plasma excitation by SFC solvents appears to be less troublesome than for typical organic HPLC solvents. It seems likely that as SFC becomes more widely adopted, element-specific detection by atomic plasma emission will become a useful option.

4. Plasma mass spectrometry in chromatographic detection

The most extensively developed plasma mass spectral analytical technique is that of ICP–MS [100–102].

The argon ICP, comprising ionized argon at 9000 K, acts as a mass spectral ion source. For a liquid sample solution, after aerosol formation in a nebulizer and passage through a spray chamber, analyte is injected into the plasma where it undergoes desolvation, vaporization, atomization and ionization. A portion of the ions are sampled from the center of the plasma through a water-cooled metal cone, separated from the greater portion of the argon and directed, through a low-pressure interface into the mass spectrometer. A typical interface reduces sample pressure from atmospheric to around 10^{-5} Torr.

ICP–MS combines the advantages of ICP–AES such as multi-element analysis, wide dy-

namic range and speed, with mass spectral acquisition, enhanced detection limits (typically 0.01–0.1 μg/l) and capability for isotopic analysis. Some factors may cause problems in general ICP–MS applications, such as solute levels, isotopic or matrix interferences. Speciation of chemical form of elements determined is also not directly accessible; it is here that interfaced sample introduction techniques incorporating separation and/or concentration provide a major analytical advantage. There is a substantial number of examples of flow injection analytical, liquid and gas chromatographic interfaces and applications for ICP–MS and a comprehensive review and bibliography of these has been presented [103].

In view of the drawbacks experienced in HPLC–AES interfacing, notably with respect to detection limits, the enhanced detectability possible with plasma mass spectroscopy has proved attractive. The techniques employed for liquid chromatographic interfacing are similar to those used in AES, most important being minimization of the volume of the interface tubing to preclude degradation of chromatographic efficiency. Careful selection of the mobile phase is required to prevent blocking of the interface or extinguishing of the plasma. Reversed-phase HPLC is most acceptable to the ICP system, increase of plasma power and possibly cooling to enhance condensation of volatile solvents being needed as the proportion of organic mobile phase components increases. Normal-phase partition or adsorption chromatographic solvents such as alkanes present considerably more difficulty for effective plasma interfacing.

As might be predicted the interfacing of GC with ICP–MS has proven simpler than for HPLC since no solvent removal techniques have to be employed with concomitant analyte losses. As discussed below the optimal elemental detection limits in chromatography are currently probably obtainable with GC–ICP–MS.

In view of the extensive GC–MIP applications already existing, the microwave-induced plasma interface has also found favor for GC interfacing. However there is a considerable potential for HPLC application of MIP–MS, notably for the non-metallic elements which are more effectively excited in helium plasma.

4.1. GC–plasma mass spectrometry

Efforts to develop interfaced GC methods have been relatively limited until recently, since GC–ICP itself has attracted little attention. However, coupling packed-column GC with ICP–MS was reported to give detection limits from 0.001 to 400 ng/s for a range of elements including halogens, silicon, phosphorus and sulfur [104]. Applications have recently been made for trace metal analysis at low pg/s levels and an example is shown in Fig. 13, which depicts a ^{120}Sn ion-selective chromatogram of tetraalkyltin compounds at low pg levels from a harbor sediment [105].

Olsen et al. have reviewed the area of chromatography–plasma-mass spectroscopy in general, and indicated both advantages and problems of the technique [106].

Evans et al. described a low-pressure ICP which can be used for both molecular and atomic mass spectrometry in the interfaced chromatographic mode [107]. Element-selective detection was obtained for lead, tin, iron, chlorine, bromine and iodine compounds in the range from 13 pg (Pb) to 500 pg (Cl). By decreasing the power and plasma gas-flow, it was possible to

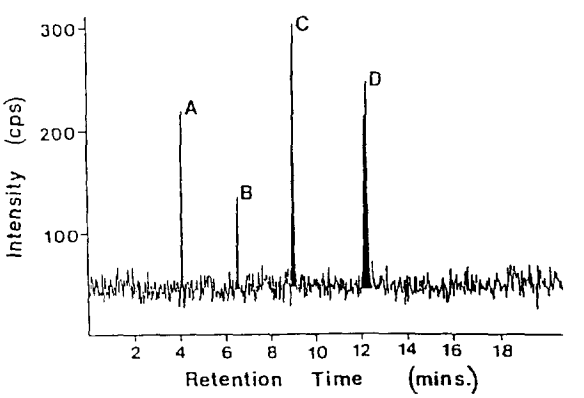

Fig. 13. ^{120}Sn ion selective GC–ICP–MS of tetraalkyltin compounds from a harbor sediment. Peaks: A = $SnEt_4$; B = $BuSnEt_3$; C = Bu_2SnEt_2; D = Bu_3SnEt.

sustain a helium plasma using only carrier gas from the gas chromatograph, and mass spectra were obtained for halogenated compounds similar to those obtained for electron-impact MS. Adjustment of the plasma gas-flow and forward power influenced the fragmentation of the organic species. Fig. 14 shows the interface used in this study and Fig. 15 depicts lead (m/z 208) and carbon (m/z 12) element-specific chromatograms of tetraalkyl lead compounds in naphtha.

4.2. HPLC–plasma mass spectrometry

One of the most sophisticated developments in plasma detection for chromatography has been the development of systems such as HPLC–ICP–MS [108] for which detection limits as low as 100 pg/peak have been obtained for many elements. Ion-exchange and ion-pair chromatography were used for speciation of triorganotin species [109] and arsenic speciation has been examined in a number of studies [110,111]. The technique shows excellent prospects in biomedical and clinical studies in which analyte levels are usually below the capabilities of ICP emission detection. Gercken and Barnes [112] interfaced aqueous size-exclusion chromatography (SEC) with ICP–MS for element and isotope-ratio detection of lead and copper in protein fractions of serum and blood cell hemolysate with molecular mass ranges from >600 to 11 kDa. Fig. 16 shows distributions of lead, copper and zinc in rat blood serum. Elder et al. [113] described detection limits in the 1–10 ppb range for metallodrugs and their metabolites, measured in samples from patients undergoing gold drug therapy for arthritis. Crews et al. [114] used SEC to monitor cadmium binding to proteins.

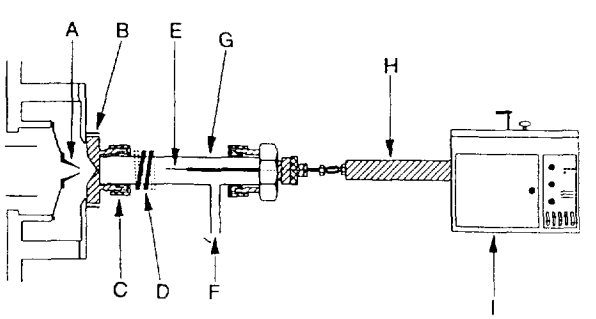

Fig. 14. GC–LP–ICP–MS instrumentation. A = skimmer; B = low-pressure sampler; C = vacuum fitting; D = ICP load coil; E = tip of GC column; F = plasma gas; G = quartz torch; H = heated transfer line; I = gas chromatograph.

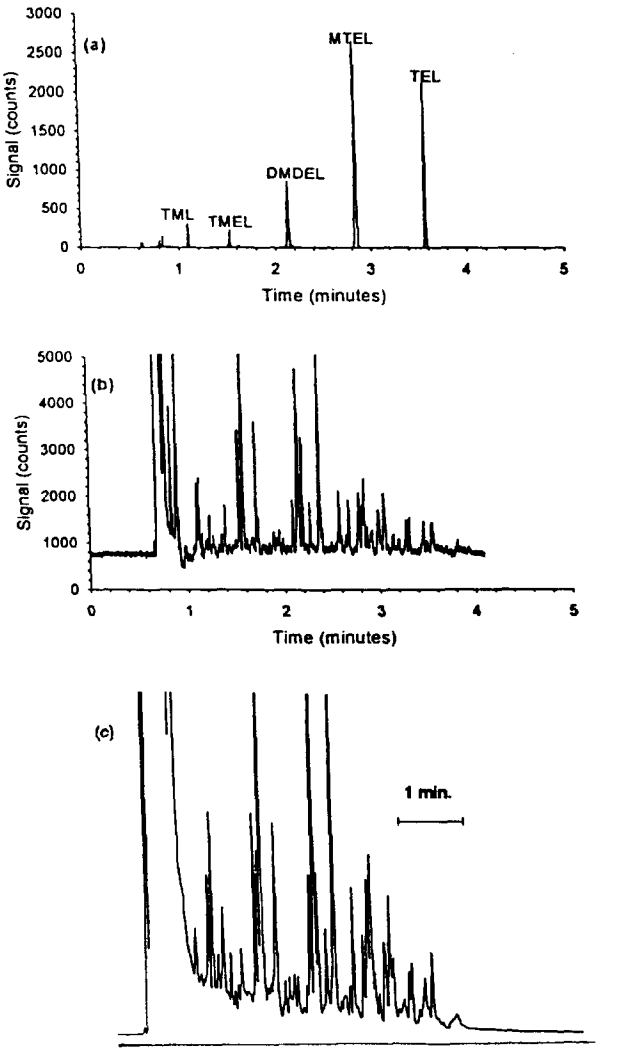

Fig. 15. Ion-selective GC–ICP–MS of naphtha in hexane containing tetramethyllead (TML), trimethylethyllead (TMEL), dimethyldiethyllead (DMDEL), methyltriethyllead (MTEL) and tetraethyllead (TEL).

The elements mercury, arsenic, lead and tin have attracted most interest from the trace element environmental point of view. Bushee obtained a 7 μg/l detection limit for mercury as methylmercury in tuna extracts [115]. Di-

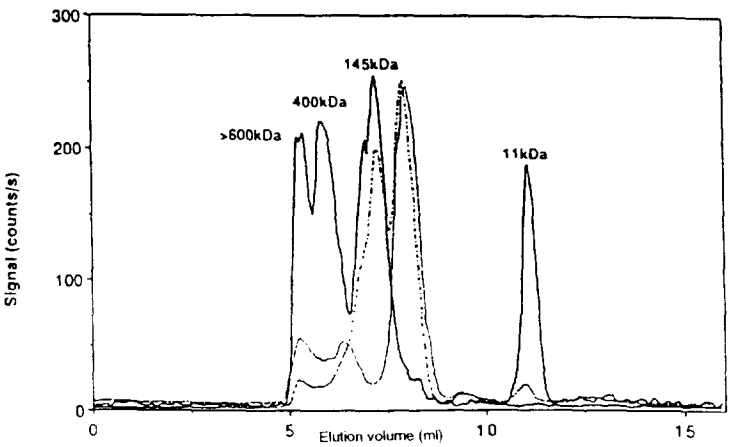

Fig. 16. Size exclusion (SEC)–ICP–MS of ^{208}Pb (– – – – –), ^{63}Cu (- · · · -), and ^{64}Zn (. . . . . .) distribution in rat blood serum. Evaluated molecular masses of lead fractions are labelled.

methylarsenic acid, monomethylarsonic acid and arsenobetaine were measured at the 50–300 pg level in fish tissues by Beauchemin et al. [116], while Arar et al. [117] have determined hexavalent chromium in sludge incinerator emissions using interfaced ion chromatography and ICP–MS, employing isotopically enriched chromium internal references.

Roychowdhury and Koropchak using thermospray LC–ICP–MS showed detection limits improved by factors of more than 25–50 compared to pneumatic sample introduction; they used ion chromatography for separation of chromium(III) and (VI) species [118]. Mason et al. [119] utilized a moving band interface and a 125 W Beenakker MIP, examining 80:20 water–methanol eluent on an ODS column for 9-chlorofluorene, *p*-chlorobiphenyl etc., obtaining Cl detection at a few 100 pg/s [119]. Takatera and Watanabe [120] used derivatization of sulfhydryl groups in chicken ovalbumin as organomercurials using different derivatization agents. Detection was at 1 pmol of ovalbumin [120]. Heitkemper et al. [121] speciated arsenic in urine, as arsenite, arsenate, dimethyl arsenite and monomethylarsonate; arsenic detection was 20–90 pg in aqueous and urine samples. Interference with arsenic at *m/z* 75 was noted from *m/z* 75 (Ar40 – Cl35) [121]. Heitkemper et al. evaluated a 300 W Beenakker for MIP–MS of halogenated compounds. Detection limits found were 50 pg for Br, 1 pg for I and 10 ng for Cl, organic solvent background being considered.

4.3. SFC–plasma mass spectrometry

Olson and Caruso [122] determined halogenated compounds with SFC–MIP–MS, obtaining compound detection limits of 100 pg and 25 pg for Cl and Br in chloro and bromonaphthalenes (15 pg for Cl and 0.75 pg absolute element). Microwave power was 120 W, a demountable torch was used and a frit restrictor; carbon dioxide was used as the mobile phase. Vela and Caruso [123] determined tri- and tetra-organotin compounds by SFC–ICP–MS, obtaining sub-pg detection limits. Effects of interface and restrictor temperatures were examined in detail as were those of mobile phase composition and pressure program [123]. Chen et al. evaluated tetraalkyl and tetraphenyltin to sub-pg limits with a 3-order of magnitude linear range by SFC–ICP–MS [124].

4.4. Miscellaneous flow monitoring plasma mass spectral methods

Closely linked to interfaced chromatography with plasma mass spectrometry are some other examples of monitored flow systems. Taylor et

al. [125] interfaced sedimentation field-flow fractionation (SFFF) with argon ICP–MS to determine trace elements in size-separated colloidal particles of less than 1 μm in diameter, in river surface water [125]. Hill et al. [126] investigated the potential of flow-injection analysis (FIA) interfacing; they injected small volumes of organic solvents into a dilute nitric acid stream, measuring levels of 1 ng/ml of trimethylgallium and methyllithium stabilized in diethyl ether [126].

5. Conclusions

The wider adoption of plasma spectral chromatographic detection depends on the availability of commercial instrumentation to permit interlaboratory comparisons of data and the development of "recommended" methods of analysis which can be widely used. Plasma chromatographic detection has already demonstrated utility in academic, governmental and industrial laboratories and the commercial introduction of an integrated GC–MIP system suggests that the future of this technique is strong, despite earlier setbacks. Fully integrated GC units which circumvent the need for analysts to interface their own chromatograph, emission device and spectrometer may become as familiar in the future as GC–MS and GC–FTIR systems are today.

The introduction of equivalent integrated HPLC–atomic emission instrumentation is more problematic since the recent focus upon plasma mass spectral detection for liquid chromatography has shown this approach to be more effective in terms of sensitivity.

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