Applied Organometallic Chemistry (1988) 2 441–450

0268-2605/88/02505441/$03.50

Trace speciation by HPLC–GF AA for tin- and lead-bearing organometallic compounds, with signal increases induced by transition-metal ions

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Received 27 April 1988 *Accepted 14 June 1988*

High-performance liquid chromatography coupled with graphite furnace atomic absorption spectroscopy (HPLC–GF AA) gives element-specific detection of environmental samples containing trace amounts of organotin or organolead species. The direct GF AA of organotin and organolead species is subject to errors arising primarily from loss of analyte prior to atomization, probably through the formation of refractory carbides and of compounds or complexes that are volatile at low temperatures. Examples abound in the literature of signal suppression in the GF AA of organometallic species in environmental samples, and several furnace tube modifications have been developed to overcome this suppression. Here, the analyte and a modifier are co-pipetted into a conventional furnace tube, from either a solution of analyte or an HPLC effluent. Oxides of transition metals (e.g. chromium, manganese, or tungsten) are shown to enhance both tin and lead signals, whereas chlorides do not, suggesting the low-temperature formation of relatively involatile metal oxides or volatile metal chlorides, respectively. In the absence of modifier, GF AA signal intensities decrease consecutively for equal quantities of mono-, di-, tri- and tetra-butyltin species, but are nearly equal for the first three in the presence of complexing dichromate ($Cr_2O_7^{2-}$). The lesser signal increase for tetrabutyltin indicates a dissimilar low-temperature complexation chemistry for the fully ligated neutral organometal to that for the ligated ions. Similar results are demonstrated in post-column addition of a matrix modifier to effluent containing either organotin or organolead species.

Keywords: Analysis, environmental species, graphite furnace atomic absorption (GF AA), high-performance liquid chromatography (HPLC), organolead, organotin, signal increase, trace speciation

INTRODUCTION

Certain manmade organotin compounds are toxic to marine species in picomolar concentrations[1] while others are essentially harmless, the toxicity depending not only on the metal but also the carbofunctional ligand structures and their number.[2] Hence, ultratrace speciation as well as metal detection is critical for estimating environmental impact. We have described the automated coupling of electrothermal atomization, or graphite furnace atomic absorption spectroscopy (GF AA) with high-performance liquid chromatography (HPLC) for element-specific trace speciation of organic compounds of tin,[3] lead,[4] and arsenic.[5,6] At regular intervals, aliquots are transferred from the effluent stream into the furnace tube and then heated in programmed steps, viz. drying, ashing and finally atomization. The measurement of organotin or organolead species by GF AA may be complicated by the loss of either analyte prior to atomization, owing to low-temperature volatilization[7,8] or possible formation of refractory tin carbides on the walls of the furnace tube.[7] In general, the accuracy and precision of measurements by GF AA depends on (1) retaining the analyte in the analytical volume while drying and ashing the sample, (2) maximizing the population of analyte vapor in the path of light during the measurement, and (3) minimizing the incidence of extraneous signals such as memory owing to deposition of analyte vapors in the cooler parts of the furnace tube.

Measures for diagnosing and eliminating such complications are vitally important in the diagnostic characterization of environmental samples. In kinetic studies of organotin release, Blair *et al.*[8] found that the level of salts in estuarine waters suppresses the tin signal severely. Parks *et al.*[9] developed a toluene extraction procedure for determining organotins in seawater and found that striking increases in signal intensity were obtained by adding to the analyte solution a matrix modifier such as potassium dichromate ($K_2Cr_2O_7$). Weiss *et al.*[5] performed arsenic-specific size exclusion chromatography on samples of shale oil, and found that post-column addition of aqueous nickel nitrate [$Ni(NO_3)_2$] gave at least twofold signal increases. Chiba[10] found that iron [Fe(III)] *suppressed* the tin-specific GF AA of biological samples; reduction of ferric to ferrous iron with ascorbic acid gave a twofold increase of signal. These results exemplify a multiplicity of suppressors that may interfere with the GF AA of complex samples, such as aqueous extracts of geological specimens for example, or liquors containing biologically solubilized ores. Deletion of a suppressor has the effect of enhancing the observed signal.

Several reports describe 'enhancement' of GF AA signals for various organometallic analytes through modification of the furnace tube surface.[7,11–16] Fritzche *et al.*[7] coated tubes by soaking them overnight in solutions of metallic salts (tungsten, molybdenum, zirconium and tantalum), and then drying and firing them prior to use for tin quantitation. With zirconium-coated furnace tubes, Vickrey *et al.*[13,14] reported fourfold increases in tin signal for Bu_2SnCl_2 and 47-fold for Me_2SnCl_2, attributing the difference between species to surface effects on the mechanism of tin volatilization. The same zirconium treatment led to marked increases in lead signal only if an interfering halide [I^-] was present. Since lead(II) iodide (PbI_2) is volatile between 990 and 1500 °C,[17] considerably less than the atomization temperature, presumably the effects of I^- are alleviated by the prior reaction of this potential ligand with the matrix modifier. Other matrix modifiers have been employed for alleviation of interference (e.g. ammonium salts, peroxides and acids[10,11,18–21]) which similarly prevent early volatilization of the analyte, e.g. as a metal dichloride or tetrachloride. L'vov[22] and others[21,23] have used platform inserts that improve signal intensities for specific elements. The volatilization of analyte is retarded owing to the fact that the platform is not heated as rapidly as the walls of the cuvette, and the effect is to maximize the amplitude of the absorption pulse. Jewett *et al.*[24] preliminarily reported 15- to 20-fold signal increases when both analyte (tin or lead species) and a salt of one of several transition metal modifiers were co-pipetted from a single solution into a furnace tube, as compared with the measurements in the absence of modifier. The metal salts were used in extremely high molar ratios *vis-à-vis* the analyte, e.g. as much as 20 000:1. Parks *et al.*[9] combined L'vov platforms with matrix modifications to obtain an additive net signal increase for ultratrace concentrations of organotin species in a toluene extract of seawater. In the present work, we have performed HPLC coupling with GF AA detection improved by similar matrix modifications. Organotin and organolead analytes in the effluent stream are mixed with an aqueous solution of ammonium dichromate prior to automated sampling; thus, analyte and modifier are co-deposited in the furnace tube prior to GF AA.

EXPERIMENTAL*

Stock solutions of the inorganic salts (analytical grade) were prepared (0.01 or 0.02 mol dm^{-3}) in deionized water. Tributyltin chloride (Bu_3SnCl), triethyllead chloride (Et_3PbCl), and tetraphenyllead (Ph_4Pb) were obtained commercially and used without further purification. Tributyltin chloride (9.95×10^{-3} mol dm^{-3}) stock solution in deionized water was diluted with aqueous ammonium citrate (0.06 mol dm^{-3}) to a final concentration of 1.0 μmol dm^{-3}. Tetraphenyllead (3.65×10^{-5} mol dm^{-3}) was dissolved in tetrahydrofuran (THF) and diluted to a final concentration of 2.92×10^{-7} mol dm^{-3}. Triethyllead chloride (1.64×10^{-5} mol) was dissolved with warming (60 °C) in deionized water and diluted with water to a final concentration of 4.1×10^{-7} mol dm^{-3}.

To prepare the chromatogram of a sample of gasoline, 10 cm^3 of leaded gasoline taken from a

* Certain commercial products or equipment are mentioned in order to describe experimental procedures adequately. In no case does such identification imply endorsement by the National Bureau of Standards, nor does it imply that the material is necessarily the best available for the purpose.

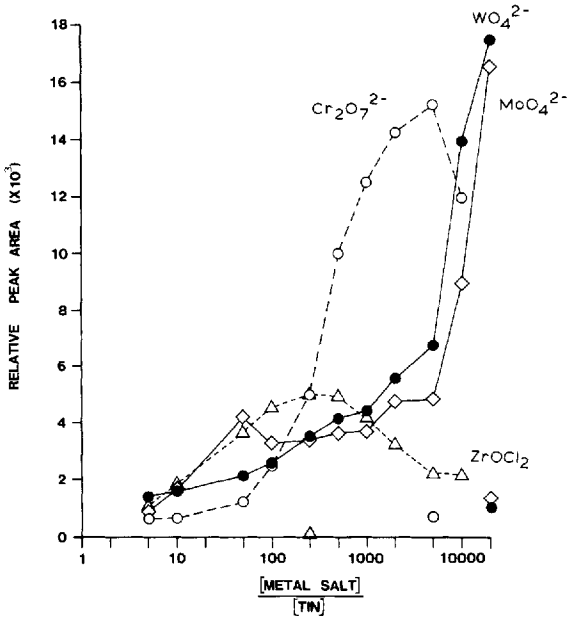

Figure 1 Increases in tin signal with concentration of transition-metal salts in aqueous solution. Tin concentration (as tributyltin) 1.2 ng per 20 μL-aliquot (0.5×10^{-6} mol dm^{-3}); modifier concentrations range from 0.5×10^{-6} to 0.5×10^{-2} mol dm^{-3}. Analysis performed with modifier solutions in order of increasing concentration; analyte excluded from the final test, showing that high concentrations of the modifiers do not add significantly to the tin signal. GF AA program A.

commercial gasoline pump was diluted to 1 dm^3 with a mixture of 98 parts of methanol and 2 parts of water.

Aliquots of each matrix modifier (M), consisting of a given inorganic stock solution, were added volumetrically to a constant volume of analyte solution (A) to obtain molar ratios ([M]/[A]) ranging between 0:1 and 20 000:1, as indicated in Fig. 1. The appropriate volume of water was added to each mixture to maintain a given concentration of analyte throughout a series of tests. For example, to 600 μL(mm^3) of a tin analyte solution (10^{-6} mol dm^{-3}) was added 30 μL of aqueous ammonium dichromate [$(NH_4)_2Cr_2O_7$, 10^{-3} mol dm^{-3}], and to this mixture 570 μL of water to give 1200 μL of solution having chromium and tin in the molar ratio of 60:1. These solutions usually were tested by GF AA (using furnace tubes of conventional design) immediately after their preparation, and in all cases within 15 min. A previously unused ('fresh') furnace tube was installed at the beginning of a series and the 0:1 sample tested first (generally with six to eight firings), followed consecutively by samples having increasingly higher concentrations of the matrix modifier. The temperature programs for both tin and lead are listed in Table 1. At the end of each series, the solution of metal of the highest concentration was tested without analyte to detect any interfering contribution to the analtye signal, and a final test was made of the analyte in the absence of modifier [([M]/[A] = [0]/[1])].

Table 1 Operating conditions for the GF AA program

	A (Sn)		B (Pb)	
Thermal program	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)
Dry	100	15	100	15
Char	600	10	600	10
Atomize	2700	7	2300	7

Furnace purge gas: argon, 200 cm^3 min^{-1} stopped-flow mode microprocessor, auto-zero background mode; integration, 8 s.
Spectral settings:
Sn: wavelength 224.6 nm, sw 0.7 nm
D_2 continuum lamp.
Pb: wavelength 217.0 nm, sw 0.7 nm
D_2 continuum lamp.

Figure 2 is a schematic diagram of the high-performance liquid chromatograph (HPLC) coupled to the GF AA. Figure 3 is a diagram of the mixing chamber C that serves as an autosampling interface. The chromatographic eluent enters the chamber from below (inlet A), the modifier through the sidearm (in-

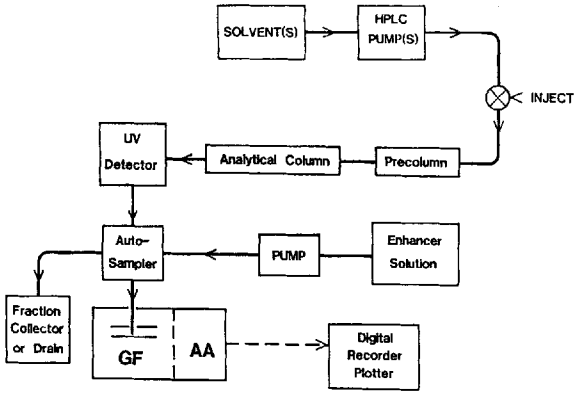

Figure 2 Block diagram for the HPLC–UV–GF AA system, designed for continuous mixing of eluent and a solution of the matrix modifier. The autosampler automatically transfers 20-μL aliquots of the mixture into the graphite furnace. The excess solution may be collected or drained off.

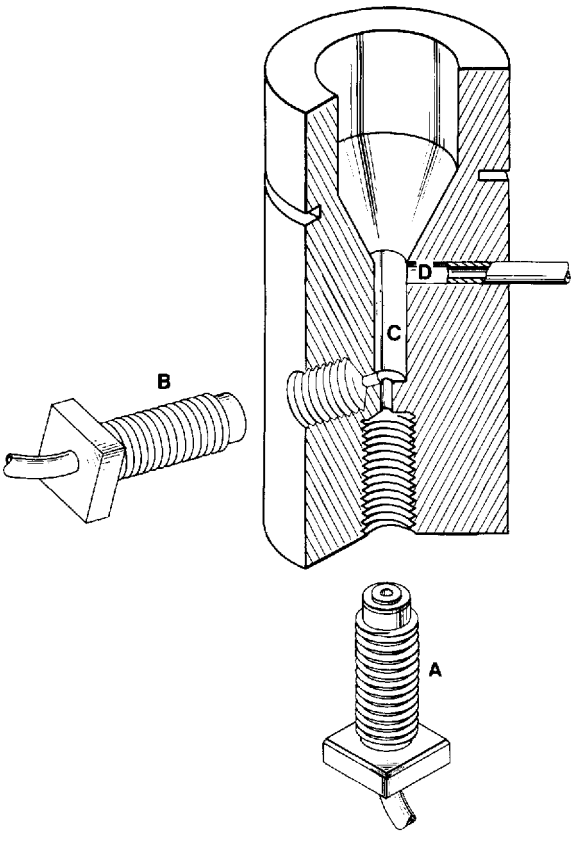

Figure 3 Post-column mixing and sampling cup. HPLC eluent flows through port A, and modifer solution through port B. Mixing occurs in reservoir C (98.7 μL in volume) below port D, which serves as the outlet to the drain.

let B), and exits to the drain through outlet D. Details of the complete HPLC–GF AA system with an in-line UV detector, autosampling interface, and digital readout peripherals have been described.[3] The autosampler pipettes aliquots into the furnace at predetermined intervals. Although we installed a fresh furnace tube prior to the beginning of each chromatogram in the present experiments, the practice would not be required in routine chromatography. Specific chromatographic parameters are presented in the legends to the figures. To demonstrate effects of ligands on signal intensities, equal concentrations of Bu_4Sn, Bu_3SnCl, Bu_2SnCl_2, and $BuSnCl_3$ were tested with and without addition of $(NH_4)_2Cr_2O_7$. The effect of post-column addition of ammonium dichromate was similarly determined by the summation of resolved peaks in the chromatogram of a mixture of tributyltin, triethyltin, and dibutyltin.

RESULTS AND DISCUSSION

Our experimental scheme (Fig. 2) is designed for continuous post-column mixing of analyte and matrix modifier. Co-deposition of a modifier and an analyte provides a controlled source of both, whereas the surface composition of preconditioned tubes may change with consecutive firings, as Vickrey reported for the case of zirconium-coated tubes.[14] Since HPLC–GF AA might require 100 or more element-specific measurements for a single injection, the quantitation of well-resolved species could be subject to continuing changes in sensitivity. We tested a number of candidate inorganic salts for absorption at 224.6 nm (Table 2), one of two strong lines for tin. The background signal at 2500 °C is negligible for salt concentrations up to 0.01 or 0.02 mol dm^{-3}, the concentration range used for all of the candidate modifiers, except for sodium molybdate.

The magnitude of the GF AA signal due to tributyltin (Table 2; 1.2 ng per 20-μL aliquot, 1.0 μmol dm^{-3}) in water (column 5) or in a mixture of water and metallic salt (column 7) varies with the modifier and its molar concentration. In the absence of any modifier, the sensitivity is poor. The average of eight readings ranges from 300 to about 800, and the relative errors are as high as 51%. Some amplification of signal is evident in the presence of every metal ion. The molar ratios of metal to analyte for highest increases range from 1600 ($NaVO_3$) to 40 000 ($Cr_2O_4^{2-}$). Decreases in the relative error are evident in every case, but vary widely from 14.8% ($MnCl_2$) to 1.34% (MnO_4^-).

These effects are depicted in Fig. 1, where summations of signal peak areas are plotted as a function of molar concentrations. Ammonium dichromate confers maximum signal increase [15 400 absorption units-second (abs-s)] at the concentration of 5×10^{-3} mol dm^{-3}, and a *weaker* tin signal is evident when the concentration is doubled. The dichromate solution of highest concentration, subsequently tested, itself gave no tin signal. With a solution of either molybdate (MoO_4^{2-}) or tungstate (WO_4^{2-}), the signal is much lower than for dichromate ($Cr_2O_7^{2-}$) at relatively low concentrations but considerably higher for a salt concentration of 10^{-2} mol dm^{-3},[1] owing to the signal repression noted above. Solutions containing zirconyl chloride ($ZrOCl_2$) confer relatively weak signal increases, reaching a low maximum at 2.5×10^{-4} mol dm^{-3}. These data indicate that chemical

Table 2 Increases in tin signals from tributyltin due to transition-metal salts

		GF AA (abs-s)					
		Modifier (no tin)		Bu_3Sn[a] (alone)		Bu_3Sn[a] (with modifier)	
Modifier	Concn (mol $dm^{-3} \times 10^{-3}$)	Avg[b]	SD[c]	Avg[b]	SD	Avg[b]	SD
$NaVO_3$	0.5	140	89	690	150	3470	330
$(NH_4)_2Cr_2O_7$	5.0	690	95	100	150	15140	400
$Cr(NO_3)_3$	9.6	125	103	770	190	11720	877
$KMnO_4$	18.2	1140	85	680	170	17070	228
$MnCl_2$	18.2	20	60	570	140	2640	390
$Fe(OAc)_2$)	17.1	95	63	700	110	5700	280
$Ni(OAc_2$	17.0	420	150	810	140	5630	250
$ZrOCl_2$	1.0	90	100	590	130	4200	160
Na_2MoO_4	20.0	37	55	330	170	16450	550
Na_2WO_4	20.0	330	70	780	130	17370	660

[a] 0.5×10^{-6} mol dm^{-3}; 1.2 ng per 20μL test aliquot. [b] $n = 6$. [c] Standard deviation.

reactions with $Cr_2O_7^{2-}$ at relatively low temperatures may result in an increased population of the gaseous analyte in the analytical beam.

Chakrabarti[25] proposed four distinct pathways for the atomization of metal salts: reduction of metal oxide by the graphite furnace; thermal decomposition of metal oxide; dissociation of oxide vapor; and dissociation of metal halide vapor. Little is known of the specific mechanisms by which low-temperature molecular pathways influence high-temperature chemistry. Figure 4 is instructive. A metal chloride ($MnCl_2$) is essentially ineffective over the concentration range, whereas permanganate (MnO_4^-) improves the tin signal as effectively as dichromate ($Cr_2O_7^{2-}$), tungstate, (WO_4^{2-}) or molybdate (MoO_4^{2-}). This suggests that the tin species are complexed with the dianions of metal oxides at temperatures below the charring temperature of 600 °C. Since tin monoxide (SnO) decomposes at 1060 °C while tin dioxide (SnO_2) melts at 1127 °C,[16] these species, if formed during the thermal decomposition of the complex, would survive the preatomization programming steps (progam A, Table 1). Furthermore, phase transformation temperatures for manganese chloride ($MnCl_2$) (melting point 650 °C) allow the coexistence of this species and tin dichloride ($SnCl_2$) (b.p. 652 °C). The formation of tin tetrachloride ($SnCl_4$) (b.p. 114 °C), however, would be consistent with the early volatilization of tin and the observed, low, GF AA signal.

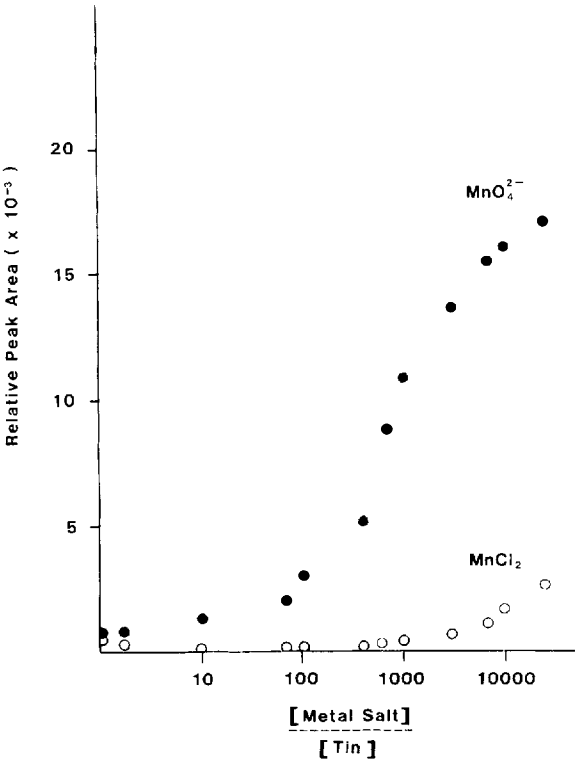

Figure 4 Increases in tin signal with concentration of potassium permanganate or manganous chloride. Tin concentration as tributyltin, 0.5×10^{-6} mol dm^{-3}. Modifier concentrations, 0.5×10^{-6}–0.5×10^{-2} mol dm^{-3}. Analysis performed with solutions of consecutively increasing modifier concentration. GF AA program A.

Table 3 Increases in lead signals for organoleads due to transition-metal salts

		GF AA (abs-s)					
		Modifier (no Pb)		Et_3PbCl[a] (alone)		Et_3PbCl[a] (with modifier)	
Modifier	Concn (mol $dm^{-3} \times 10^{-3}$)	Avg[b]	SD	Avg[b]	SD	Avg[b]	SD
$NH_4Cr_2O_7$	4.1	155	33	405	125	6930	170
Na_2MoO_4	4.1	1120	65	540	130	2120	1000
Na_2MoO_4	4.1	506	250	1495	340	6000	240
				Ph_4Pb[c]		Ph_4Pb[c] + modifer	
$(NH_4)_2Cr_2O_7$	4.1	12	20	740	230	2120	220
				Bu_4Pb[d]		Bu_4Pb[d] + modifier	
$(NH_4)_2Cr_2O_7$	4.5	80	45	2050	170	3910	370
Na_2MoO_4	4.1	–	–	–	–	1840	240
Na_2WO_4	4.1	–	–	–	–	2140	55

[a] Triethylead chloride, 4.1×10^{-7} mol dm^{-3}; [b] $n = 6$. [c] Tetraphenyllead, 4.1×10^{-7} mol dm^{-3}. [d] Tetrabutylead, 4.1×10^{-7} mol dm^{-3}.

Ammonium citrate was added to these solutions to volatilize any free halides[18] through the formation and decomposition of ammonium halide (NH_4X) into volatile products (ammonia, HX). But ammonia would not necessarily interfere with the low-temperature formation of a $(MnCl_2)_2$:Sn complex, or with the transfer of bound chlorine to tin. The data in Table 2 suggest that the maximum signal for 1.2 ng of tin is obtained in a solution having any of the three dianions of metal oxides, owing to the most efficient retention of the analyte as a complex with the dianion in the analytical volume.

Organolead species

Table 3 and Fig. 5 refer to GF AA determinations of organolead species at a concentration of 1×10^{-7} mol dm^{-3}, with dichromate, tungstate and molybdate at concentrations ranging from 10^{-7} to 10^{-4} mol dm^{-3}. Except for molybdate dianions, the effect of the modifier is very similar to the case of organotin species, with a much greater increase in lead signal for triorganolead, for example, than for tetraorganolead species. Again, the data imply that relatively low-temperature events preceding volatilization of the ligands are critical for maximization of the analyte signal.

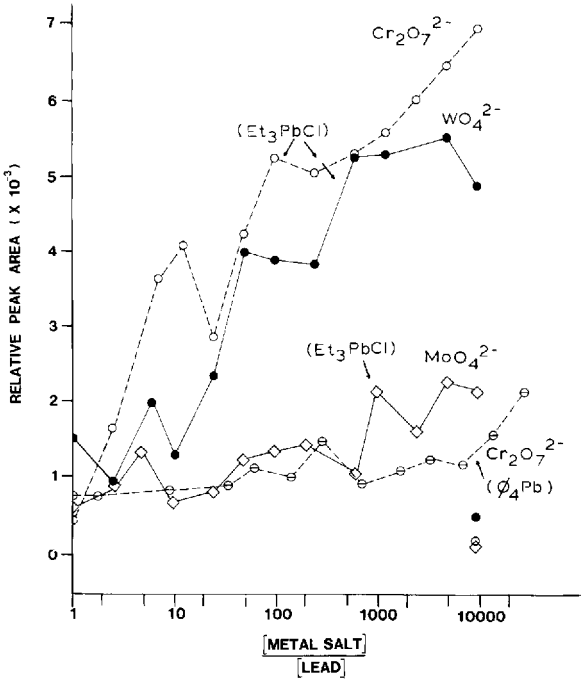

Figure 5 Increases in lead signal with concentration of transition-metal modifiers in aqueous solutions. Lead concentration (as organolead) 4.1×10^{-7} mol dm^{-3}. Modifier concentrations, 4.1×10^{-7}–4.1×10^{-3} mol dm^{-3}. Analyte excluded from final tests, showing that high concentrations of modifier do not add to the lead signal. GF AA program B.

HPLC–GF AA of organotin species

For improvements in HPLC–GF AA detection (schematic diagram presented in Fig. 2) we employed a stream of aqueous ammonium dichromate having a concentration of 0.0075 mol dm^{-3}, which entered the post-column mixing chamber at the controlled flow rate of 0.25 cm^3 min^{-1}; hence the mixture contained 0.0025 mol dm^{-3} of dichromate in the chamber per analysis. With conventional GF AA, tin species of different ligand number, e.g. Bu_4Sn, Bu_3Sn^+, Bu_2Sn^{2+}, and $BuSn^{3+}$, gave signals of very different intensity. Prior to HPLC, we were particularly interested in verifying the report[16] that matrix modifiers are capable of diminishing or eliminating this difference to provide a 'levelling' effect. In cup tests using pyrolytically coated furnace tubes of conventional design, 1.0 ng specimens of tin in aqueous solutions, and no modifier (Table 4), $BuSn^{3+}$ gave the highest GF AA signal; Bu_2Sn^{2+} and Bu_3Sn^+ showed no significant difference; and Bu_4Sn gave the weakest signal by far. With conventional tubes, the same relationship continued to hold when dichromate was used as a modifier. For tetrabutyltin, the use of L'vov platform tubes, however, resulted in tin signals much higher than those obtained in the presence of dichromate. With conventional tubes and no dichromate, either 1.0 ng or 0.2 ng of tin as tetrabutyltin gave a signal intensity about 19 % of that of monobutyltin, compared to 60 % when using L'vov tubes.

Figure 6 represents strong cation exchange (SCX) chromatograms of a mixture of tributyltin, dibutyltin, and triethyltin, with and without matrix modification. Summation of the GF AA signals[3] is indicated in Table 5. Again, the extent of increase in signal varies considerably, owing to differences in the signal inten-

Table 5 Relative intensities of HPLC–GF AA peaks for Bu_2SnCl_2, Et_3SnCl and Bu_3SnCl with or without modifier

	Summation of peaks	
Species	No modifier	Modifier
Bu_3SnCl[a]	1390	15700
Et_3SnCl[b]	1640	16100
Bu_2SnCl_2[a]	7100	15400

[a] 40 ng tin injected. [b] 50 ng tin injected.

Table 4 Effects of matrix modification on the intensity of tin signals for butyltin species

		Analytical matrix							
		L'vov[a]				Conventional[b]			
		Modifier		No modifier		Modifer		No modifier	
Species	Sn (ng)	Avg.[a]	SD	Avg.[c]	SD	Avg.[c]	SD	Avg.[c]	SD
Bu_4Sn	1.0	37400	5400	22400	1170	9470	4000	1840	730
	0.4	23000	2250	—	—	—	—	—	—
	0.2	12600	750	—	—	—	—	—	—
Bu_3SnCl	1.0	46200	3500	29300	1380	37100	2660	4200	180
	0.4	35600	560	—	—	—	—	—	—
	0.2	14000	870	—	—	—	—	—	—
$Bu_2Sn^2Cl_2$	1.0	51000	2000	30200	2700	38700	900	3720	500
	0.4	26500	160	—	—	—	—	—	—
	0.2	15300	1000	—	—	—	—	—	—
$BuSnCl$	1.0	57100	1900	37500	2700	49000	570	6000	510
	0.4	36900	1870	—	—	—	—	—	—
	0.2	20500	840	—	—	—	—	—	—
Blank	—	4400	750	3900	700	3400	700	980	280

[a] Platform tubes (21). [b] Pyrolytically coated tubes. [c] $n = 7$.

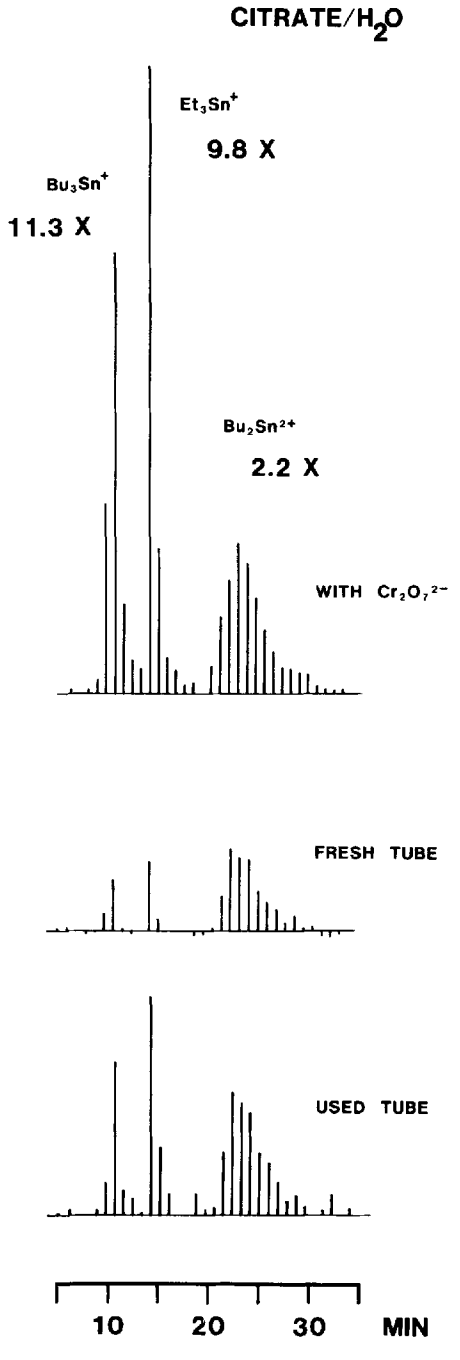

Figure 6 HPLC chromatograms of a mixture of tributyltin chloride, triethyltin chloride, and dibutyltin chloride; as tin, 40 ng, 50 ng, and 50 ng, respectively, per 20-μL injection. Column, strong cation exchange (SCX), 10 μm particle size, 25 cm × 4.6 mm i.d. Eluent methanol:water (70:30) containing 0.08 mol dm^{-3} ammonium citrate. Flow rate 0.5 cm^3 min^{-1}. Post-column addition of either water or aqueous $Cr_2O_7^{2-}$ (0.0075 mol dm^{-3}) flowing at 0.25 cm^3 min^{-1}. GF AA program A.

sity of each species in the absence of modifier. When the modifier is used, the signal intensities agree within experimental error.

HPLC–GF AA of organolead species

Figure 7 represents the reverse-phase (C_{18}) HPLC chromatogram of a sample of leaded gasoline, as received from a commercial gasoline dispensing pump. The assignment of peaks is based on theoretical retention parameters which depend on the calculated total molecular surface areas (TSA) of the respective, eluted species.[28] Consistent with the results of our cup tests (Table 3) are the relatively low increases in signal obtained for tetraethyllead, methyltriethyllead, and dimethyldiethyllead. Greater increases in signal intensity occur for the unknown species whose retention volume corresponds to that of trimethylethyllead and tetramethyllead. This suggests alternative assignments, e.g. cationic species such as methyldiethyllead ($MeEt_2Pb^+$) and dimethylethyllead (Me_2PbEt^+) having the same surface areas as the respective tetraorganolead species. Unfortunately these species were not available to us as authentic compounds during the research.

CONCLUSIONS

The element-specific HPLC–GF AA of organotin and organolead species is subject to errors arising from low-temperature phenomena which greatly diminish the quantity of analyte actually measured at the temperature of atomization. However, when oxides of transition metals are co-pipetted with analyte into a GF AA furnace tube, the observed signal may be greatly increased, owing apparently to the low-temperature formation of stable complexes between the oxide and the analyte. Post-column addition of the metal oxide to an effluent stream bearing mono-, di-, or tri-butyltin cations results in large signal increases. Tetrabutyltin is less amenable to signal increases. Summation of HPLC–GF AA peaks shows the net signal is proportional to the tin concentration for each of the cations and a weaker net signal is obtained for tetrabutyltin. Similar results are obtained with organolead species. This 'levelling' effect has major implications for the assessment of biological transformations of organometallic species in the environment, such as the degradtion of toxic tributyltin to non-toxic di- and mono-butyltins in marine environments.

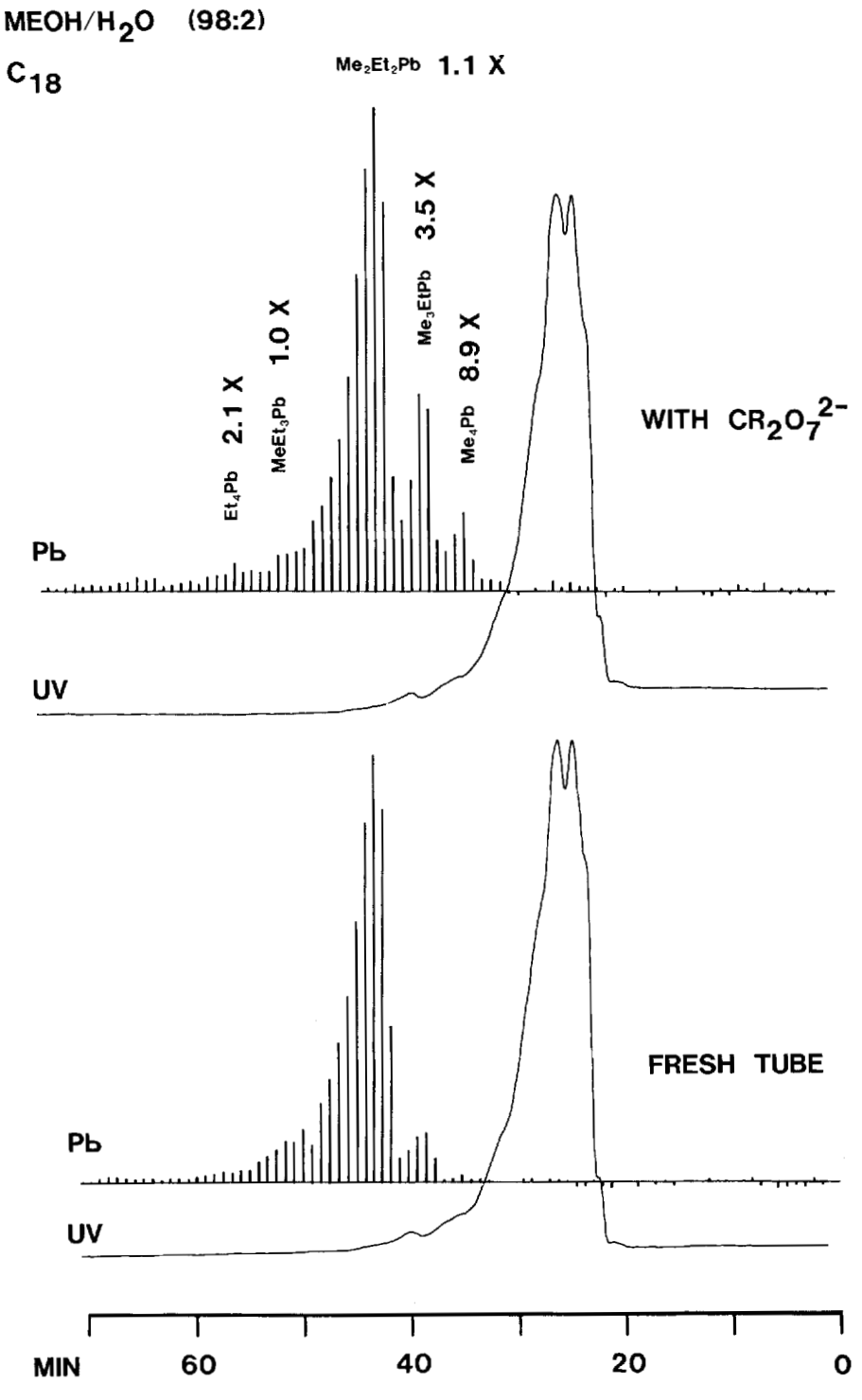

Figure 7 HPLC chromatogram of commercial gasoline diluted 10 times with methanol:H_2O (98:2). Injection volume 20 μL. Column C_{18}; particle size 10 μm; 25 cm × 4.6 mm i.d. Eluent methanol:water (98:2) flowing at 0.2 cm^3 min^{-1}. Post-column addition of either water or 0.01 mol dm^{-3} $Cr_2O_7^{2-}$ flowing at the rate of 0.2 cm^3 min^{-1}. Organolead peak assignments based on total surface areas of respective species (two). GF AA program B.

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