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Interference from Elemental Sulphur in the Determination of Organotins by Gas Chromatography with Flame Photometric Detection

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Elemental sulphur, a common constituent of marine sediments, has been shown to give dialkyl sulphides with the Grignard reagents commonly used to derivatize alkyltin species before their determination by gas chromatography with flame photometric detection (GC–FPD). Further, it has been demonstrated that even with the red filter for 610 nm (normally used for organotin compounds) fitted to the detector, sulphur compounds do give rise to an emission signal, which may be mistaken for tin emission from a pentylated or propylated alkyltin compound, as the respective retention times are in some cases quite close. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Gas chromatography has become the established technique for the determination of organotins in environmental samples for two good reasons: pentylation allows all the butyltins, and many other alkyltins too,[1, 2] to be determined in one procedure with quite short run times (Fig. 1); and the flame photometric detector fitted with a red filter centred on 610 nm makes possible a reasonable working range with good sensitivity, excellent tolerance to hydrocarbons, and high selectivity for organotins.[3] Hydridization has been the method of choice for very sensitive detection of the butyltins with purge-and-trap chromatography coupled to a flame photometric detector,[4, 5] but ethylation, originally via a Grignard reaction[6] and more recently by reaction with sodium tetra-ethylborate, is now becoming the preferred method for the determination of butyltins in environmental samples,[7] while hexylation has been coupled with supercritical fluid extraction (SFE) sample clean-up for the determination of butyl- and phenyl-tins.[8]

In an earlier paper[9] we described the chromatographic behaviour of a range of mixed alkyltins, and demonstrated the possibility of determining butyltins and methylbutyltins in sediment and fish samples. However, a recent

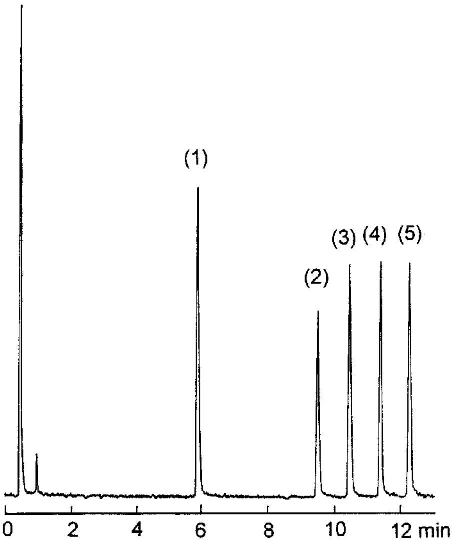

Figure 1 GC trace of butylin standards using FPD with a 610 nm filter: (1) Bu_2Me_2Sn; (2) Bu_4Sn; (3) Bu_3PeSn; (4) Bu_2Pe_2Sn; (5) $BuPe_3Sn$.

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survey carried out by the authors of some sediment samples from a number of sites known to have had a past history of contamination by tributyltin, some from a polluted estuary and others from a stream polluted by a spillage of wood-treating chemicals, threw up some questions for which answers were not apparent. Why, for instance, should residues of butyltins *apparently* be found a substantial distance *upstream* of a spill site, as well as downstream? Why should tetrabutyltin always seem to be present in significant amounts compared with the tri- and di- and mono-butyltin species? Any why should some contaminated sediment samples appear to have substantial levels of methylbutyltin and others not?

We have attempted to answer these questions by subjecting some marine sediment extracts, after pentylation with the appropriate Grignard reagent, to analysis by gas chromatography–mass spectrometry. The results, which were rather unexpected, are reported in this paper.

EXPERIMENTAL

Apparatus

Shimadzu GC-8 capillary chromatograph with a flame photometric detector, fitted with either a blue filter (390 nm maximum transmission) or a red filter (610 nm maximum transmission, from Infrared Engineering Ltd) and with a 12 m × 0.53 mm BP-1 column was used with a temperature programme of 80–250 °C at 10 °C min^{-1}.

A Carlo Erba model HRGC 5160 capillary chromatograph with a Hewlett-Packard mass selective detector and fitted with a 25 m CP-Sil 19 column has also used with a temperature programme of 80–250 °C at 10 °C min^{-1}.

Procedure for extraction of organotins from sediments

Wet sediment (20–25 g) was placed in a 200 ml all-glass container such as a wide-necked reagent jar with a ground-glass lid and 40 ml of distilled water were added, followed by 60 ml of concentrated hydrobromic acid. The vessel was closed and shaken several times, each time for 1–2 min, allowing it to stand and the contents to settle for 5–10 min between shaking. The mixture was extracted with two successive 25 ml portions of 0.05% (w/v) tropolone in diethyl ether; each portion of ether was decanted, after the solids had settled, into a 250 ml separating funnel. The (lower) aqueous phase was separated and discarded; then the ether phase was run into a beaker containing anhydrous sodium sulphate to remove the water. Finally, the ether phase was transferred to a three-necked round-bottom flask and the solvent volume was reduced to 3–5 ml by means of a rotary evaporator.

Procedure for derivatization of butyltins

A 5 ml aliquot of the Grignard reagent (1 M pentylmagnesium bromide in diethyl ether) was added to the preconcentrated sample extract or to an ether solution of appropriate organotin standards, optionally with dimethyltin dichloride as internal standard, and the mixture was refluxed at 40 °C with continuous stirring for 1 h, using a small water bath on a stirrer–hotplate.

The mixture was allowed to cool, then the excess of the Grignard reagent was destroyed by careful dropwise addition of approximately 5 ml of 0.5 M sulphuric acid. The solution was transferred to a separating funnel and the aqueous phase was run off and extracted in a second funnel with two 5 ml portions of pentane. The combined ether–pentane solution was washed with 25 ml of 3% (m/v) sodium hydroxide, then concentrated either using a rotary evaporator or simply by blowing a stream of nitrogen gas over the surface of the liquid. Finally, the solution was made up to an appropriate volume, dried over anhydrous sodium sulphate, and analysed by gas chromatography.

RESULTS AND DISCUSSION

The alkyltin standards give very characteristic mass spectra, showing the pattern of the seven major stable isotopes, with atomic masses from 116 to 124 amu (Fig. 2).

The molecular ion at *m/z* 362 for the tributylpentyltin molecule containing the most abundant isotope, ^{120}Sn, is absent due to splitting off of a butyl group (*m/z* 57) or of a pentyl group (*m/z* 71), giving rise to ions at *m/z* 305 and 291 respectively. The relative intensities of the *m/z* 305 and 291 peaks help one to distinguish the different mixed butylpentyltins from one

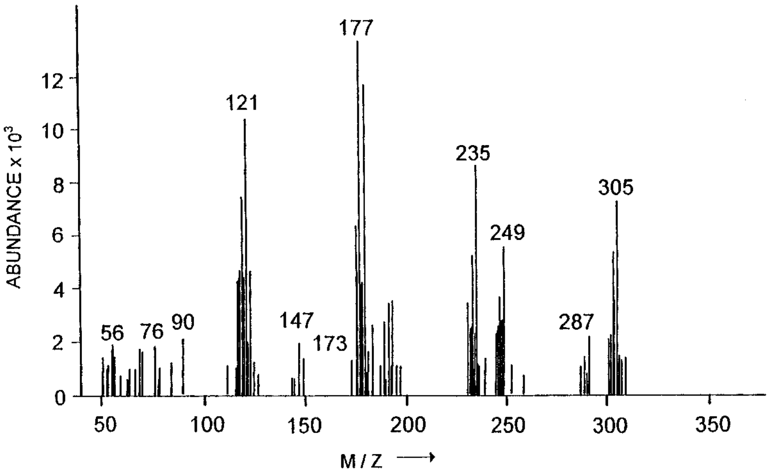

Figure 2 EI–MS spectrum of Bu_3PeSn obtained with the GC–MS instrument.

another:[10] the three-fold-higher probability of losing a butyl group than the one pentyl group results in a (more than) three-fold-higher intensity of the *m/z* 305 peak. The next fragmentation step has a still higher chance of losing a butyl group, so that the next fragments of *m/z* 249 for BuPeSnH and *m/z* 235 for Bu_2SnH are of nearly equal intensity. The fragment at *m/z* 179 for $BuSnH_2$ has acquired two hydrogen atoms after losing the alkyl groups.

Some extracts of estuarine sediments known to have been contaminated with butyltins were also analysed by GC–MS, giving traces of which Fig. 3 is typical. One large chromatographic peak, at $t_R = 5.51$ min, which was recorded from many sediment samples and is labelled (1) in Fig. 3, turned out *not* to belong to an organotin at all, but to be due to dipentyl sulphide, and at least

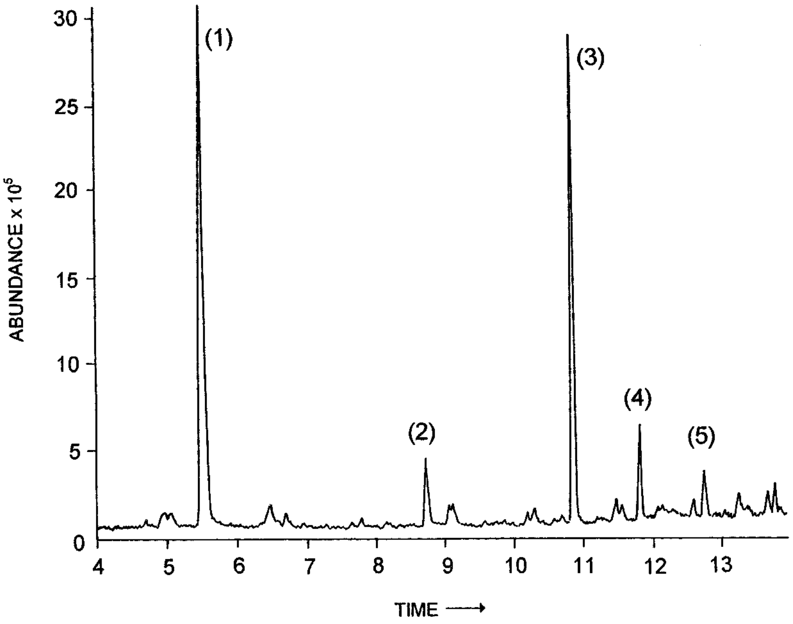

Figure 3 Total-ion GC–MS trace for pentylated estuarine sediment extract: (1) Pe_2S; (2) Pe_2S_2; (3) Bu_3PeSn; (4) Bu_2Pe_2Sn; (5) $BuPe_3Sn$.

two smaller peaks could now be assigned to dipentyl disulphide [$t_R = 8.73$ min, labelled (2) in Fig. 3] and dipentyl trisulphide ($t_R = 11.68$ min). The problem now concerned the origin of these compounds.

Sulphur in the elemental state is a common constituent of sediments, particularly of marine sediments. Indeed, removal of elemental sulphur from sediment extracts is an important step in the determination of organochlorine residues.[11] Elemental sulphur arises as a result of the activities of two families of bacteria: first the sulphur-reducing bacteria *Desulphovibrio*, which convert sulphate under anoxic conditions (common in sediments) to sulphide, and second, the oxidizing *Thiobacillus oxidans* which convert sulphide to elemental sulphur.[12]

The second question concerned the nature of the products of reaction between elemental sulphur and pentylmagnesium bromide. A small portion (a few milligrams) of elemental sulphur was therefore taken through the pentylation procedure and the resulting solution was analysed by gas chromatography–mass spectrometry. Several products were identified by comparison of the mass spectra with those in the NIST library, as well as with the spectra recorded on the same instrument by subjecting known standards to chromatography under the same conditions. Major peaks in the chromatogram were due to dipentyl sulphide, dipentyl disulphide and dipentyl trisulphide, as had been found in the extract of the polluted estuarine sediment.

This same mixture, from the pentylation of elementary sulphur, was then run on the chromatograph with the flame photometric detector. With the red filter (610 nm) normally used for organotins, small peaks were obtained (Fig. 4), the identities of which were confirmed from their retention times as being the same three pentyl sulphides found in the sediment extracts. When a blue filter (390 nm) was fitted in place of the red one, very much stronger signals were recorded (Fig. 5), as would be expected for a series of organosulphur compounds.

Reaction with propylmagnesium bromide, which can also be used for derivatization of butyltins, produces a similar family of organosulphurs (Fig. 6) with appropriately shorter retention times. This chromatogram shows also a typical broad peak for the large excess of elemental sulphur which had not been derivatized. In all of these chromatograms (Figs 4–6) the width of the peaks was due to overloading of the capillary column by the amount of sulphur taken.

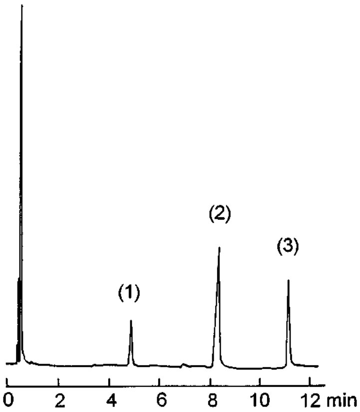

Figure 4 GC–FPD trace of products of reaction between pentylmagnesium bromide and elemental sulphur: red filter (610 nm) (tin mode): (1) Pe$_2$S; (2) Pe$_2$S$_2$; (3) Pe$_2$S$_3$.

The identities of the previously unknown reaction products following derivatization of sediment extracts, and also the absence of these peaks in the chromatograms from standards prepared from pure butyltin salts, as in Fig. 1, were thus explained.

Interference from sulphur in the determination of organotins

The possibility of interferences in the determination of organotins due to elemental sulphur in the original sample has now to be considered. The retention time of at least one of the pentylation

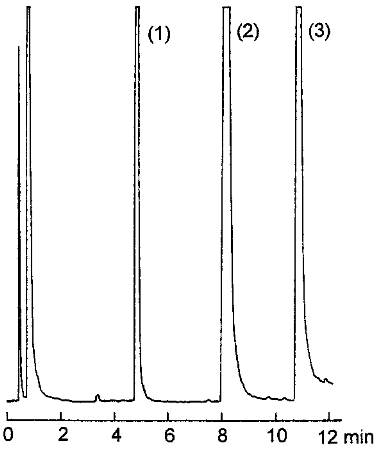

Figure 5 GC–FPD trace of products of reaction between pentylmagnesium bromide and elemental sulphur: blue filter (390 nm) (sulphur mode): (1) Pe$_2$S; (2) Pe$_2$S$_2$; (3) Pe$_2$S$_3$.

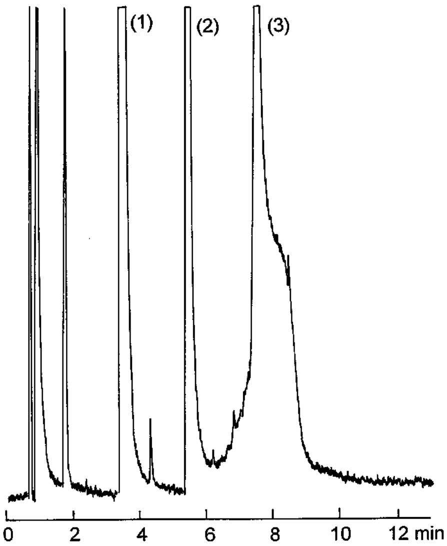

Figure 6 GC–FPD trace of products of reaction between propylmagnesium bromide and elemental sulphur: red filter (610 nm) (tin mode): (1) Pr_2S; (2) Pr_2S_2; (3) Pr_2S_3.

products (dipentyl trisulphide) lies very close to that of one of the pentyltins (dibutyldipentyltin), as can be seen in Table 1, and another (dipentyl disulphide) comes rather close to tetrabutyltin. It seems likely that the presence of alkyltins in a sediment could (wrongly) be deduced from peaks in a chromatogram which are in fact due, *not* to alkyltins, but to alkylsulphur compounds. Table 2 gives the retention times for the corresponding propyl derivatives. Here there is less probability of overlap between sulphur and tin compounds, as the propyl sulphides are more volatile than the corresponding pentyl compounds.

The possible interferences occasioned by closeness of retention time are summarized in Tables 3 and 4 as Kovats retention indices for the relevant substances, determined by comparison of the retention times with those of C_{12}–C_{20} n-alkanes run on the same columns with the same temperature programmes. The propyl sulphides were not analysed by GC–MS on the CO-Sil-19 column. Though the FPD has a poor sensitivity to hydrocarbons, adequate signals (about ten times the noise level) could be obtained from injection of 2.5 μl of a solution of 1000 $\mu g\ ml^{-1}$ of each n-alkane, enabling the retention indices to be calculated for the column in the FPD instrument. These data provide a useful extension to those published earlier[9, 13] for mixed alkyltin compounds. The sensitivity of the FPD with the red filter is about 250 times less for hydrocarbons than it is for organotins.

It is apparent that Pe_2S_3 elutes very shortly before Bu_2SnPe_2, with the likelihood of mistaken identity, and similarly for Pr_2S_2 and Bu_3SnPr. However, as long as the peaks are correctly identified, quantitation of the organotins is still possible with the FPD in the presence of much greater amounts of the sulphur compounds. Concentrations of 100 $\mu g\ ml^{-1}$ of dipentyl sulphide in a derivatized extract had no significant effect at the 95% confidence level on the peak heights recorded from any of the butylphenyltins in the range 5–100 $\mu g\ ml^{-1}$.

Response and selectivity of the flame photometric detector

The flame photometric detector, proposed originally for the sensitive and selective detection of

Table 1 Retention times (min) of some pentylsulphur and butylpentyltin compounds

	Column				
Tin compound	BP-1, 12 m		CP-Sil 19, 25 m		Sulphur compound
		4.90		5.51	Dipentyl sulphide
Dimethyldipentyltin	5.97		6.26		
		8.30		8.73	Dipentyl disulphide
Tetrabutyltin	9.52		9.82		
Tributylpentyltin	10.47		10.85		
		10.98		11.58	Dipentyl trisulphide
Dibutyldipentyltin	11.01		11.83		
Butyltripentyltin	12.26		12.76		

Table 2 Retention times (min) of some propylsulphur and butylpropyltin compounds

Tin compound	Column BP-1, 12 m	 CP-Sil 19, 25 m	Sulphur compound
	3.45	—	Dipropyl sulphide
	5.41	—	Dipropyl disulphide
Tributylpropyltin	5.52	6.68	
Dibutyldipropyltin	6.13	7.73	
Butyltripentyltin	6.72	8.73	
	7.50	—	Dipropyl trisulphide

organosulphur compounds,[14] has been thought to be very selective for tin when fitted with a red (610 nm) filter.[4] However, Olson *et al*., reported as long ago as 1983 that flame photometric detection following purge-and-trap sample preparation followed by hydride generation with sodium borohydride gave peaks for dimethyl sulphide and dimethyl disulphide even in the tin mode with the red filter.[5] A recent paper, describing a supercritical fluid extraction of organotins followed by derivatization with hexyl groups,[8] reported the formation of hexyl sul-

Table 3 Retention indices for butylpentyltin compounds and pentylsulphur compounds

Tin compound	Retention indices BP-1	 CP-Sil-19	Sulphur compound
	1290	1295	Dipentyl sulphide
Dimethyldipentyltin	1345	1355	
	1595	1610	Dipentyl disulphide
Tetrabutyltin	1648	1663	
Tributylpentyltin	1738	1752	
	1820	1830	Dipentyl trisulphide
Dibutyldipentyltin	1825	1835	
Butyltriphentyltin	1910	1915	

Temperature programme: (both columns) 80-250 °C at 10 °C min^{-1}.

Table 4 Retention indices for butylpropyltin compounds and propylsulphur compounds

Tin compound	Retention indices BP-1	 CP-Sil-19	Sulphur compound
	1190	—	Dipropyl sulphide
	1430	—	Dipropyl disulphide
Tributylpropyltin	1440	1430	
Dibutyldipropyltin	1515	1510	
Butyltripentyltin	1585	1590	
	1690	—	Dipropyl trisulphide

Temperature programme: (both columns) 80-250 °C at 10 °C min.

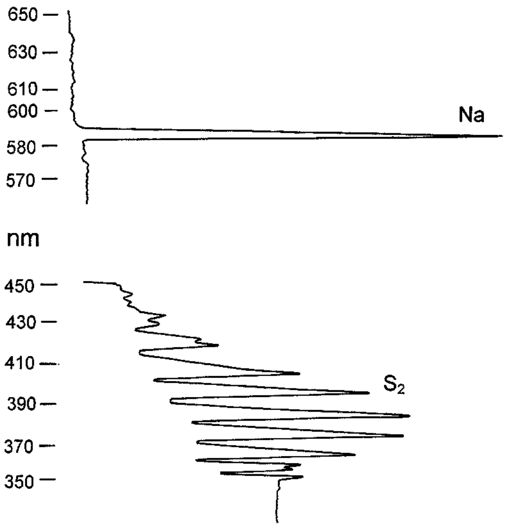

Figure 7 Emission spectrum from S_2 in a fuel-rich air–hydrogen flame. Note absence of any emission at 610 nm. the line at 589 nm is from sodium.

phides in the derivatized extracts, but did not propose any explanation.

The sulphur molecular emission spectrum

The emission band centred at 390 nm, from molecular sulphur in a cool hydrogen–entrained air flame (fig. 7), is well known.[15] The emission spectrum from such a hydrogen flame, with argon as support gas into which was bled a small flow of SO_2, was recorded using a Unicam SP 9 atomic absorption spectrometer switched to the emission mode, covering the range 350–650 nm. The band in the violet/blue, though not very intense, is well defined, with fine vibrational structure, but there is clearly nothing at all in the red.

An interference filter centred around 610 nm should not transmit a significant level of light of wavelength 390 nm. Indeed, the transmittance of the 610 nm filter supplied by Infrared Engineering Ltd, and used in this work, measured at 390 nm, was less than 0.1%. As the signals from sulphur compounds measured with the red 610 nm filter was attenuated only about eight-fold compared with their signals recorded with the blue 390 nm filter, one is forced to conclude that there must be emission from sulphur in this cool hydrogen flame at 610 nm.

A characteristic feature of the sulphur calibration graphs with the flame photometric detector is the square-law response attributable to the formation, from sulphur atoms, of the light-emitting molecular S_2 dimer in the flame. If the emission in the red is due to S_2, it also should exhibit this effect. The response of the detector to the red emission, measured as peak height, for several alkylsulphur compounds was recorded for 3, 10, 30 and 100 ppm of each compound dissolved in pentane, using the red and then the blue filters. The slopes of the log–log plots for dipentyl trisulphide were 1.83 (red filter) and 1.88 (blue filter) (Fig. 8), typical of slopes for other organosulphur compounds with the blue filter, but the actual intensities in the red were, as found before, considerably less than those in the blue. It does seem, then, that the emission in the red is also from the dimeric S_2 molecule.

The question of why organosulphur compounds give an emission signal from the FPD fitted with the red filter is not easily answered. Originally it seemed possible that residues of tin, deposited on the stainless steel burner tip or on the quartz liner tube surrounding the flame during combustion of organotins in previous samples, could be mobilized in the presence of a volatile organosulphur compound eluting from the column. Such deposition of tin (or the oxide), especially on the quartz tube,[16] does help to explain the severe tailing of organotin peaks which is so often observed: it is interesting that the tailing has been overcome by Donard *et al.*, by using a graphite burner jet instead.[17] In our experience, however, cleaning the burner jet

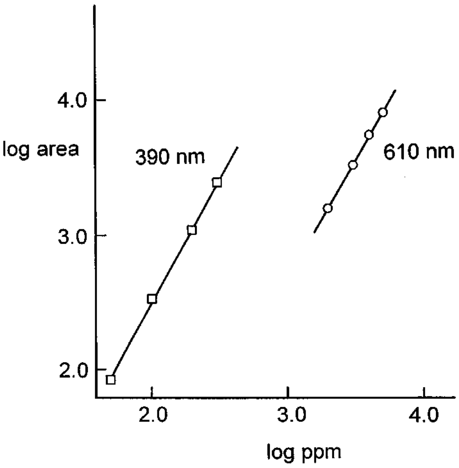

Figure 8 Log–log calibration plots for dipentyl-disulphide at 390 and 610 nm. Slopes are 1.88 and 1.83 respectively.

simply increased the sensitivity to tin (by a factor of two) without affecting the response to sulphur. Even a new stainless steel burner jet, never previously exposed to organotin compounds, gave the same response to sulphur compounds as did the old jet. Deposition of tin is not the answer.

The nearly square-law response of the detector to sulphur when the 610 nm filter is fitted is strong evidence that it is S_2 which is being observed, and possibly we should conclude that the spectrum shown in Fig. 7 must have been recorded from too hot an air/hydrogen flame, and does not give a true picture of the emission from the very low-temperature flame of the gas-chromatographic detector.

Response of the FPD with the 390 nm filter to alkyltins

The calibration set of organotins used to give the chromatogram in Fig. 1 was run again, but this time with a blue (390 nm) filter fitted. The peaks were a little higher than those recorded with the red filter, but the background noise was significantly greater, so the limit of detection was not as good. However, the slopes of the log–log graphs were, for both filters, close to unity, as we would expect for tin. Table 5 summarizes response data for several organotin compounds with the two detector filters, in all cases for 100 ng of tin injected on-column.

The flame photometric detector in the sulphur mode (390 nm) has been proposed for the determination of organotins, with a rather poorer sensitivity (by a factor of 0.65) than when used at 610 nm.[18] We have shown previously that it is also possible to work with no filter, but that the signal-to-noise ratio is then much worse and this offsets the apparent gain in sensitivity.[9] The relative sensitivity is, however, as much a function of the red sensitivity of the photomultiplier and the transmission of the filters, as of the tin emission, so the ratios of the signals cannot really be said to be in disagreement.

CONCLUSIONS

It appears, then, that typical levels of elemental sulphur in sediments can give rise to peaks suggesting the presence of small concentrations of certain alkyltins. Approximately 5 μg of sulphur injected on-column was found to give a signal similar to that obtained from 50 ng of tributyltin under the same conditions, with the red filter. We suggest that when such low levels of unknown organotins are ‘found’ in a sediment, the chromatogram should be run again, but with the blue filter fitted. As Fig. 8 shows, the response to alkyltins should be extremely small, so any peaks recorded with the blue filter will probably be due to organosulphur compounds. (Organophosphorus compounds are less likely to be present.) The conclusions based on the peaks recorded with the 610 nm filter may then have to be reconsidered.

However, the tolerance of this method to concomitant sulphur, using pentylation following ether extraction of an acidified sediment, is one small advantage compared with the recently advocated hydride generation GC–AA approach[19] in which high levels of sulphur in the sediment are reported to interfere with the production of the alkyltin hydrides.

Another approach to the determination of organotins is to use a capillary chromatograph coupled to a microwave plasma emission detector.[20] Though proposed many years ago,[21] this has only recently become successful with the advent of reliable commercial equipment, and offers the advantage that only atomic emission is observed from the plasma, and that use of a grating monochromator allows the tin line at 303 nm to

Table 5 Sensitivity data for some alkyltin compounds (peak heights for 100 ng on-column, arbitrary units) using the flame photometric detector

	Compound			
Filter	Bu_4Sn	Bu_3SnPe	Bu_2SnPe_2	$BuSnPe_3$
Red, 610 nm	346	364	343	350
Blue, 390 nm	416	474	466	460

be measured without interference from sulphur. The lack of selectivity of low-temperature optical emission sources giving molecular emission is clearly a disadvantage, but for most workers it is offset by the much lower price of an FPD compared with that of the MIP detector.

The authors would therefore like to draw the attention of other researchers using the flame photometric detector to the fact that not all peaks recorded using a red filter may be due to organotin compounds, and that organosulphur compounds can also give a response under these conditions.

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