Comparison of Metal-Sensitive Flame Ionization and Carbon-Sensitive Flame Ionization Detectors for the Gas Chromatographic Determination of Organotins

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A hydrogen atmosphere flame ionization detector (HAFID) which is sensitive to metal-containing compounds is compared with a traditional flame ionization detector (FID) which is sensitive to carbon-containing compounds for the determination of organotins. It was found that the HAFID is not significantly more sensitive for tin compounds than the FID. Its principal advantage over the FID is that it has a tremendous selectivity against hydrocarbons, which permits the determination of small quantities of organotins in the presence of large quantities of organic material. Selectivity of the HAFID was found to be a function of the temperature of the precombustion zone of the flame where an organic compound is apparently oxidized prior to entering the flame, reducing its ionization efficiency in the flame. Example chromatograms of responses in the two detectors are shown for the analysis of marine paint for bis(tributyltin) oxide (TBTO) and of apple tree leaves for triphenyltin hydroxide (Duter) and tricyclohexyltin hydroxide (Plictran).

Analysts interested in organotin analyses are fortunate to have such a variety of reliable detection methods from which to choose. Electron capture, flame photometry, flame ionization, conductivity, and atomic absorption spectrometry have all been employed successfully in the determination of trace quantities of organotins after gas chromatography (GC). Moreover, detectors utilizing these phenomena are often available in analytical laboratories even though they may not have been purchased specifically for the determination of organotins. The problem in selecting a GC detector for organotin analysis is often not which detector to purchase but rather which detector in the laboratory to modify. Simple removal of the interference filter from a flame photometric detector will produce an extremely sensitive tin detector (1). Interfacing an atomic absorption spectrometer to a GC is a more formidable task but provides an element specific detector which can be tuned for tin. Also, moderate organotin selectivity can be gained from an unmodified electron capture detector, and the Coulson conductivity detector has been used to selectively determine halide derivatives of organotins (2). When selective detection methods are not available, analysts often employ the catholic response of the flame ionization detector (FID) and rely upon high-resolution separations to eliminate matrix interferences.

This paper describes an organometallic selective detector which has been converted from a standard FID and evaluates this detector for the determination of organotin compounds. Both the standard FID and this modified FID, called a hydrogen atmosphere flame ionization detector (HAFID), are similar in that response originates from ions produced in a small flame of hydrogen and oxygen. Ions are extracted by an electric field from these flames, or their afterglow regions, before recombination with counterions or diffusion to ground occurs. The two detectors differ in that the FID is a hydrogen-fed diffusion flame burning in an air atmosphere while the HAFID is an air-fed diffusion flame burning in a hydrogen atmosphere.

The exact sequence of gas-phase reactions which leads to ion products is not well understood in either flame system. Some evidence recently published suggests that the ionization mechanism for normal hydrocarbons may be similar in the two detectors even though ionization efficiencies differ greatly (3). In this study the two detectors are compared to identify and define similarities and differences in their responses for organotin compounds.

EXPERIMENTAL SECTION

Instrumentation. The entire study was performed on a Hewlett-Packard 5830A gas chromatograph equipped for on-column injection with 6 ft × $^1/_4$ in. o.d. (2 mm i.d.) borosilicate columns. Packing materials employed throughout these studies varied with separation requirements and are given when individual experiments and analytical procedures are discussed below. The chromatograph was operated as recommended by the manufacturer with the exception that one of the dual FIDs which were supplied with the instrument was converted to a HAFID.

Conversion of a carbon-sensitive FID to a metal-sensitive HAFID, which has been described elsewhere (4), is simple and inexpensive. The principal differences between the two detectors are the position of the collector electrode above the flame, the flow patterns of hydrogen and air, and the addition of small amounts of silane in the hydrogen of the HAFID. For the FID, the common procedure of introducing hydrogen into the carrier gas (in this case helium) between the column and the detector was employed, while air was brought directly into the detector housing. For the HAFID, these flow patterns were reversed with O_2 being added to the air supply to produce O_2-rich air. By use of a gas cylinder which had been purchased to be 1% silane in hydrogen, mixtures of silane in hydrogen at the parts-per-million level could be prepared by varying the mixing rate of the doped hydrogen with pure hydrogen. Unless otherwise stated, gas flows were as follows: helium carrier gas = 30 mL/min, FID air = 240 mL/min, FID hydrogen = 60 mL/min, HAFID hydrogen = 1600 mL/min (1% silane in hydrogen = 5 mL/min), HAFID air = 120 mL/min, and HAFID oxygen = 150 mL/min. For all gases except hydrogen, flow measurements were made with a soap bubble flow meter. For hydrogen a displacement method of 1 L of water was employed.

Detector Evaluation Procedure. Ionization detectors in chromatography are often described and evaluated by calculating response data in terms of sensitivity, selectivity, and minimum detectable quantity. Although each of these values is related to the other, they emphasize individually important aspects of the detector's response. In this study the following definitions and equations were applied.

Sensitivity was defined as coulombs response/mole of standard injected while selectivity was considered to be the ratio of sensitivities of the organotin standard to a hydrocarbon standard. To the analyst, the minimum detectable quantity (MDQ) is perhaps the most important measurement in evaluating a detector's response. Commonly defined as that quantity of compound that will produce a maximum peak height response 2 times the noise level of the detector, it is an indication of both the sensitivity and the stability of a detector.

FID/HAFID Comparisons. Comparisons of the FID and HAFID were conducted by injecting varying quantities of rep-

Table I. Chromatographic Conditions

compound	oven temp, °C	detector temp, °C	inj port temp, °C	column packing
tetraethyltin (TET)	65	225	200	Superpak 20 M
hexabutylditin (HBDT)	245	250	225	3% SE 30
diallyldibutyltin (DADBT)	142	250	225	Superpak 20 M
bis(tributyltin) oxide (TBTO)	170	260	250	3% SE 30
tetrabutyltin (TBT)	170	250	225	3% SE 30
tetra-n-propyltin (T-n-Pt)	150	250	225	3% SE 30
dodecane	120	250	225	3% SE 30
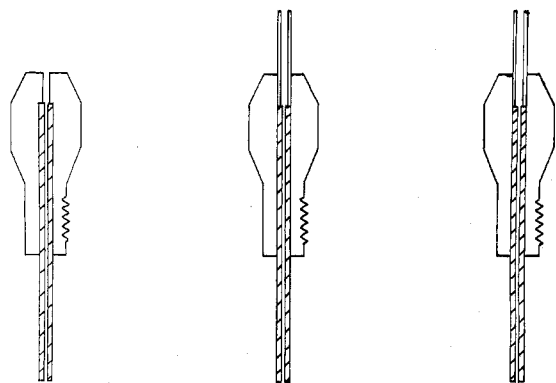
Hewlett·Packard   Stainless Steel   Quartz

Figure 1. Comparison of a modified Hewlett-Packard jet, a stainless steel jet, and a quartz jet.

resentative organotin standards into the GC. These standards were tetrabutyltin (Aldrich Chemical Co., Milwaukee, WI), tetra-n-propyltin, hexabutylditin, diallyldibutyltin, tetraethyltin, and bis(tributyltin) oxide (Alfa Division, Ventron Corp., Danvers, MA). Dodecane (Sigma Chemical Co., St. Louis, MO) was chosen as the standard representative of normal hydrocarbons. Reagent-grade hexane was used as the solvent in the preparation of a range of concentrations so that a desired quantity of standard could be introduced into the GC with a 1-μL injection. Solutions were prepared from 1 μg/μL to as low as 1 pg/μL by successive dilutions in the sequence 1 μg/μL, 0.5μg/μL, 0.2 μg/μL, 0.1 μg/μL, 0.05 μg/μL, etc. Chromatographic conditions varied somewhat for each of the standards and are summarized in Table I.

Selectivity Studies. Selectivity of organotins with respect to hydrocarbons was investigated as a function of modifications to the flame jet of the HAFID. Under normal HAFID operation, the tip of the commercial flame jet was drilled out from an internal diameter of 0.5 mm to 1 mm and to a depth of 7 mm as is shown in Figure 1. The use of a 1 mm i.d. in the flame jet of the HAFID virtually eliminates solvent flameout which can otherwise be a serious operating difficulty. For these studies, the jet was further widened at the tip and a 1 mm i.d. stainless steel or quartz tube inserted, friction tight, into the opening. These new jet tips protruded 10 mm above the exit of the original jet. The collector electrode was also moved up 10 mm to maintain a constant jet tip collector distance. Selectivities for these three jets were obtained with standards of tetraethyltin and dodecane. Chromatographic conditions and the experimental procedures were the same as those given in Table I.

Applications. To evaluate the potential of the HAFID as a method for the analysis of real samples, we analyzed paint and pesticide residue samples for organotins.

Bis(tributyltin) Oxide (TBTO) in Marine Paint. TBTO was determined in number 1130 white marine paint (Petit Paint Co., San Leandro, CA). Standards of TBTO were prepared in acetone. The paint sample was prepared by extracting 1.4483 g of paint with four 20-mL aliquots of acetone, centrifuging the combined extract to eliminate solid material, and diluting to 100 mL. An injection of 1.0 μL was then made into the GC for both the FID and the HAFID.

Chromatographic conditions were as follows: one column, packed with 3% SE-30 packing, was exchanged between the FID and the HAFID position. In each case, the oven was temeprature

programmed from 80 °C where it was increased at a rate of 5 °C/min until 6 min and then 20 °C/min to a final temperature of 250 °C.

Triphenyltin Hydroxide (Duter) on Apple Tree Leaves. Leaves collected from apple trees which had been recently sprayed with Duter were extracted with cyclohexane. The extract was then processed in a manner similar to that described by Wright, Lee, and Booth (5) in which a Grignard reagent was used to form methyltriphenyltin. The sample was then concentrated to 40 mL. Methyltriphenyltin (Alfa Products, Ventron Corp., Danvers, MA) standards were prepared in hexane. The sample and standards were chromatographed by using a 3% SE-30 column that was programmed from 120 °C after a hold time of 1 min to 250 °C at 10 °C/min. A 1-μL sample was injected for the FID, while a 1-μL sample, diluted 40 times, was injected for the HAFID.

Tricyclohexyltin Hydroxide (Plictran) on Apple Tree Leaves. Apple tree leaves which had been treated with Plictran were derivatized according to the method described by Gauer, Seiber, and Crosby (2). In this procedure the extraction and derivatization were essentially accomplished in one step by sequentially adding a solution of HBr and then benzene to the flask containing a known quantity of the leaves. After thorough mixing and separation of the aqueous and organic layers, the benzene was decanted, the aqueous layer and leaves were extracted with benzene twice more, and the combined benzene was dried over anhydrous Na_2SO_4 and concentrated to 10 mL. The result was a solution of benzene containing the brominated derivative of tricyclohexyltin hydroxide, tricyclohexyltin bromide. Tricyclohexyltin bromide (Alfa Products, Ventron Corp., Danvers, MA) standards were prepared in benzene. A Superpak 20M column was used with the following temperature program: an initial temperature of 150 °C with an initial isothermal period of 1 min and then a programmed rate of 10 °C/min to a final temperature of 250 °C. The amount injected was 1 μL of the benzene solution for the FID, while a 1-μL sample, diluted 10 times, was injected for the HAFID.

RESULTS AND DISCUSSION

Sensitivity. Initial investigations compared minimum detectable quantities, selectivities, and sensitivities of the HAFID and FID for a variety of volatile organotin compounds along with one hydrocarbon compound, dodecane. Responses were obtained at several concentration levels throughout the linear range of each detector. Table II provides detector evaluation data in which the MDQ was calculated when the response was less than 100 times the noise level. Selectivity and sensitivity values are an average of all responses obtained within the linear range of the detector.

Comparison of MDQ values often provide the most practical information on detectors because they are not only a function of the sensitivity but also of the detector's noise level and of interferences which may be encountered under certain operating conditions. However, MDQs can be misleading since they can be manipulated by varying chromatographic conditions. For example, MDQ can be decreased significantly by employing chromatographic conditions with small capacity factor (K') values. In this study MDQs were optimized for the lowest values obtainable with the HAFID. Because of the high discrimination of this detector against hydrocarbons, lower K' values could be used with the HAFID than with the FID due to less interference from the solvent peak. This effect is illustrated in Figure 2. MDQ values reported for these

Table II. Response Evaluation

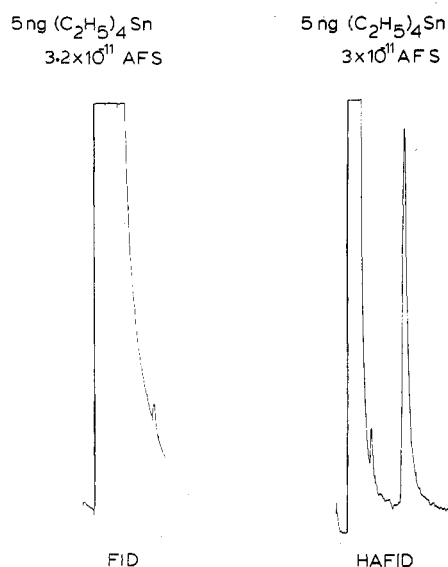|	MDQ, pg		sensitivity, coulomb/mol		selectivity	
standard	FID	HAFID	FID	HAFID	FID	HAFID
dodecane	300	48000	1.4	0.034	1.00	1.00
diallyldibutyltin	800	800	0.38	12	0.27	3.5×10^2
tetraethyltin	2000	38	0.52	29	0.37	8.5×10^2
tetrabutyltin	250	70	1.8	31	1.3	9.1×10^2
tetra-n-propyltin	1400	22	1.4	38	1.0	1.1×10^3
hexabutylditin	760	13	2.1	55	1.5	1.6×10^3

Figure 2. Chromatogram comparing solvent peak interference in the FID and HAFID. Identical conditions for both, run isothermally at 65 °C. Hewlett-Packard jet was used.

standards are near the optimum values that can be expected for the HAFID while in the FID they vary somewhat, depending upon the amount of interference from the solvent. The use of capillary columns would be expected to significantly lower the MDQs reported here.

Sensitivities are also reported in Table II. The FID behaved much as was expected. Standards containing the most carbon atoms provided the greatest sensitivity. The exception to this trend was diallyldibutyltin in which the sensitivity was considerably lower than expected for a compound with 14 carbon atoms. However, even in the HAFID its response was considerably lower than that for other organotin compounds. Perhaps its lower sensitivity might have been due to something other than detector causes, such as chromatographic instability, but further investigation was not attempted.

Excluding diallyldibutylin, sensitivities obtained for organotin in the HAFID indicate that response is primarily a function of the number of tin atoms in a molecule. The hydrocarbon standard provided an extremely low sensitivity of 0.034 coulomb/mol, almost 50 times less than in the FID. For monotin standards, sensitivities averaged about 33 coulomb/mol ±15%. This is about 25 times larger than was obtained for these compounds in the FID. For the ditin standard, hexabutylditin, sensitivity was improved about 67% over that of the monotin compounds.

The difficulty in using sensitivities as a means of comparing detectors is that they are not necessarily a true indication of how well the detector will perform under actual laboratory conditions. For example, if the sensitivities for tetrabutyltin are compared, it would seem that the HAFID could detect quantities about 17 times smaller than the FID. But MDQs for the two detectors show that only quantities about 3.5 times less can be seen with the HAFID. This descrepancy is a result

Table III. Sensitivity to Noise Ratios

	log (sensitivity/noise)	
compound	FID	HAFID
dodecane	14.2	11.2
TET	13.7	14.2
TBT	14.2	14.2
TPT	14.1	14.3
DADBT	13.6	13.8
HBDT	14.3	14.5

of variations in the noise levels of the two detectors. The average noise for the FID was about 1.0×10^{-14} A, while in the HAFID it was about 1.9×10^{-13} A.

Perhaps a detector comparison value which would be more helpful in evaluating the analytical utility of GC detectors would be the sensitivity to noise ratio since this value is independent of chromatographic conditions and reflects the limitation of detector noise. Units of this term are physically meaningless, s/mol, but its analytical utility may be of considerable value. These detector constants are listed in Table III.

In general all of these ratios for the HAFID were the same or slightly larger than those of the FID. The only value significantly different between the two detectors is the hydrocarbon value, which is much smaller for the HAFID. This then helps to explain why even though the HAFID is so much more sensitive than the FID for tin compounds, its MDQ is only slightly lower. It should be noted that this detector evaluation ratio is not completely independent of column and chromatographic effects. In Figure 2, where both detectors are run under the same conditions, both sensitivity and the MDQ in the FID are affected by interference from the solvent peak.

Selectivity. The last two columns in Table II compare selectivity values for the two detectors. In both cases dodecane was used as the standard by which selectivity was judged. As expected, selectivity for the FID averaged around 1, varying from 0.27 to 1.5. These variations were primarily a function of the number of carbon atoms in the molecule. In the HAFID, selectivity was considerably larger, ranging from 350 to 1600. These selectivity values agreed reasonably well with those obtained earlier in experiments on organoleads using this same detector (4). Yet, they were not as high as those initially reported for the HAFID (6), and a series of investigations was initiated to improve the selectivity of this detector.

As has been shown from the data presented in Tables II and III, selectivity is obtained in the HAFID not so much from enhancement in ionization efficiency over that which can be obtained in the FID but rather for the large decrease in ionization efficiency of hydrocarbons. This decrease in response is believed to be due to an oxidation step which occurs in the O_2-rich precombustion zone of the HAFID and not in the H_2-rich precombustion zone of the FID. Reductions in carbon sensitivity has been noted in the FID when small amounts of oxygen are doped into the carrier gas flow (7).

Table IV. Jet Tip Comparison

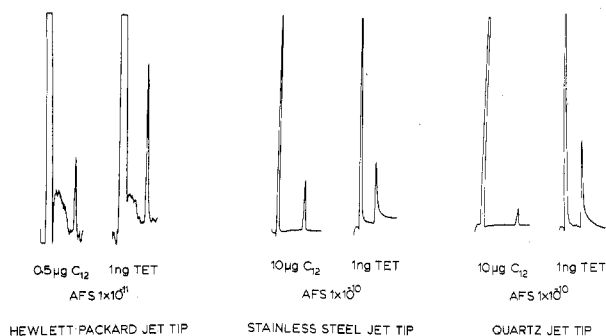|	Hewlett-Packard jet tip		stainless steel jet tip		quartz jet tip	
	MDQ	selectivity	MDQ	selectivity	MDQ	selectivity
TET	38 pg	110	15 pg	1.2×10^4	10 pg	5.9×10^4
C_{12}	48 ng	1	$0.2 \mu g$	1	$0.5 \mu g$	1

Figure 3. Chromatograms comparing the three jets for response of tetraethyltin and dodecane. Identical conditions used for both detectors. Tetraethyltin was run isothermally at 105 °C and the dodecane was run isothermally at 120 °C. Hewlett-Packard jet was used.
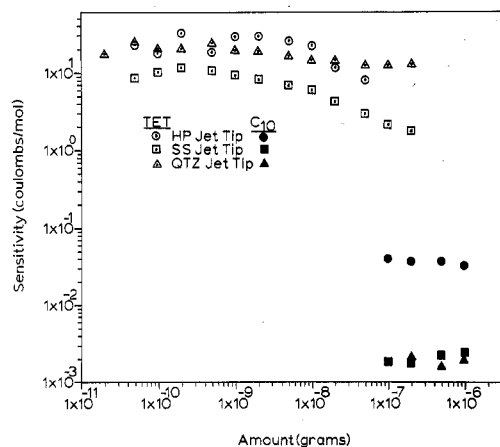

Figure 4. Plot of sensitivity vs. amount injected of tetraethyltin and dodecane for the three different jets.

For this investigation, it was postulated that the massive Hewlett-Packard flame jet was conducting sufficient heat away from the precombustion zone of the flame to decrease oxidation of the organic compound. Thus, the jet tip was modified with quartz or stainless steel tubing as shown in Figure 1 to reduce cooling and enhance oxidation.

Results of these modifications are pictured in Figure 3 and tabulated in Table IV. The response of dodecane can be seen to decrease as the flame jet is changed from the Hewlett-Packard design to the stainless steel tube and then to the quartz tube. Apparently, as the flame jet material becomes less capable of conducting heat away from the precombustion zone, the hydrocarbon is more completely oxidized before entering the flame and does not ionize as efficiently. Tetraethyltin, on the other hand, exhibited an increase in response, indicating that the mechanism of ionization for organotins is considerably different from that of hydrocarbons. It should be noted that the internal diameters of the jet tips and electrode heights were held constant throughout the study. However, configurational differences between the Hewlett-Packard jet and the stainless steel or quartz jet may have had some effect on response.

Figure 4 shows the results of this study more comprehensively with plots of sensitivities as a function of amount injected. The straight line portion of the curve indicates the linear range while the position of a line indicates the sensitivity
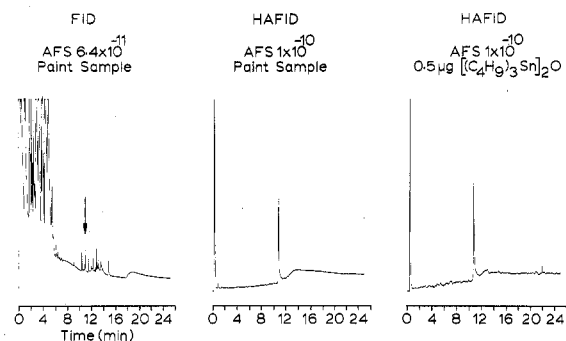

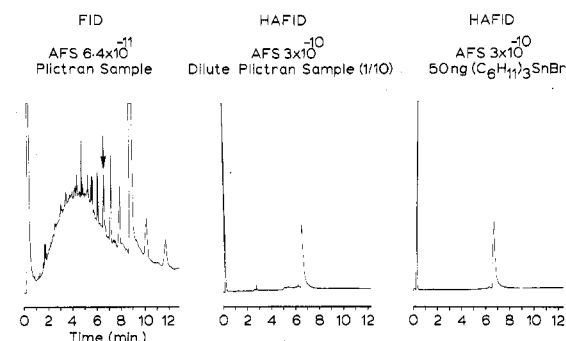**Figure 5.** Chromatograms of the paint sample for FID and HAFID.

Figure 6. Chromatograms of the derivatized plictran sample for FID and HAFID.
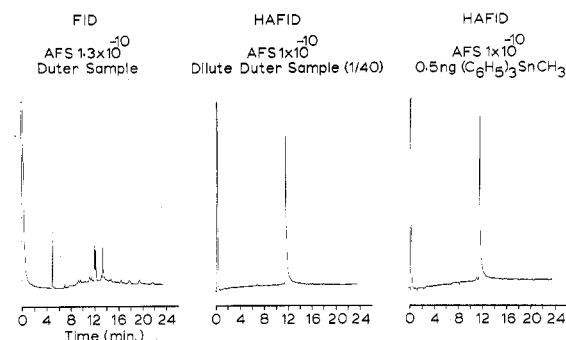

Figure 7. Chromograms of the derivatized Duter sample for FID and HAFID.

of one configuration relative to another. While the quartz jet proved to be slightly more sensitive and selective than the stainless steel jet, the convenience of the nonfragile nature of the latter is preferred in the routine operation of this detector.

Applications. Figures 5–7 illustrate applications of the two detectors for organotin determinations in several different matrixes. The analysis shown in Figure 5 is of antifouling marine paint in which bis(tributyltin) oxide (TBTO) is used as the active agent. It is clear from the chromatograms that the advantage of the HAFID is in its tremendous selectivity toward organotin compounds. This analysis was extremely simple. A portion of the paint was extracted with acetone and 1 μL of this extract was injected into the GC. The TBTO content was determined to be about 3.73% by weight of the paint, which is a little more than half of the 6.91% reported by the manufacturer. The difference may be due to degra-

861

dation of the TBTO and some loss to the glass walls of the container. While this determination of TBTO is not necessarily a trace technique, it serves to illustrate the ease and convenience of analysis on the HAFID.

Environmental analysis is an important area in which organotin analytical methodology can be applied. For example, one of the most widely used miticides in the fruit industry is Plictran, a product of the Dow Chemical Co., which contains tricyclohexyltin hydroxide as the active ingredient. Figure 6 shows the results of an analysis of apple orchard leaves for tricyclohexyltin hydroxide in which the organotin was converted to the bromide derivative and determined as tricyclohexyltin bromide. Figure 7 shows a similar analysis of a fungicide, Duter (Haywood Chem. Co., Kansas City, KS), which contains triphenyltin hydroxide, in which the organotin was converted to the methyltriphenyltin derivative using a Grignard reagent prior to injection into the GC.

Uses of organotins are expanding an industry and agriculture as they replace more toxic chemicals as pesticides, preservatives, stabilizers, etc. But with increased production comes increased danger of environmental contamination. Whether for process control or environmental monitoring, the need for quantification and identification of specific organotin compounds is growing in importance. Modification of a FID to a HAFID offers the analyst an inexpensive option for the sensitive and selective detection of organotin compounds.

LITERATURE CITED

(1) Aue, W. A.; Flin, C. G. *J. Chromatogr.* **1977**, *50*, 1435.
(2) Gauer, W. O.; Selber, J. N.; Crosby, D. G. *J. Agric. Food Chem.* **1979**, *22*, 252.
(3) Wagner, J. H.; Lillie, D. H.; DuPuis, M. D.; Hill, H. H., Jr. *Anal. Chem.* **1980**, *52*, 1614.
(4) DuPuis, M. D.; Hill, H. H., Jr. *Anal. Chem.* **1979**, *52*, 292.
(5) Wright, B. W.; Lee, M. L.; Booth, G. M. *HRC CC, J. High Resolut. Chromatogr. Chromatogr. Commun.* **1979**, 189.
(6) Hill, H. H., Jr.; Aue, W. A. *J. Chromatogr.* **1976**, *122*, 515.
(7) Sternberg, J. D.; Gallaway, W. S.; Jones T. L. *Gas Chromatogr.* (*U.S.*), **1962**, 231–267.

Spectrophotometric Determination of Iron(II) Ferrozine Complex for the Indirect Determination of Phosphate

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Phosphate in parts-per-billion amounts is determined indirectly by use of the iron(II) ferrozine complex and measuring the absorbance at 562 nm after the extraction of 12-molybdophosphoric acid into isobutyl acetate and reduction of molybdate by amalgamated zinc in 1.44 M hydrochloric acid and reoxidation of molybdenum(III) to -(VI) with iron(III). Phosphate in Environmental Protection Agency and natural water samples is determined in amounts as low as 4 ppb in the final solution, with a relative precision of 6% at 1σ value. The apparent molar absorptivity for this method is 9.66×10^5 compared to the theoretical value of 10.8×10^5.

Analytical methods for the determination of microamounts of orthophosphate are usually based on the formation of 12-molybdophosphoric acid from phosphate and excess molybdate in acid solution, and subsequent extraction of the 12-molybdophosphoric acid from excess molybdate by oxygen-containing organic solvents. The extraction is followed by an absorbance measurement of the yellow 12-molybdophosphoric acid or the reduced blue heteropoly compound. Different reducing agents have been reported in literature such as stannous chloride (1, 2), ferrous ammonium sulfate (3, 4), ascorbic acid (5, 6), hydroquinone (7), hydrazone sulfate (8), 2-amino-4-chlorobenzenethiol hydrochloride salt (9), and 1-amino-2-naphthol-4-sulfonic acid (10, 11).

Different methods for the phosphate determination have been used to overcome interferences due to arsenate, silicate, and germanate. With these methods interferences have been eliminated by using a suitable organic solvent which selectively extracts 12-molybdophosphoric acid into the organic phase and leaves interfering species in the aqueous phase (12–16). Other methods for removal of interferences include controlling hydrogen ion concentration (17, 18), preliminary volatilization of the interfering species as bromides (19), and differences in the rate of formation of heteropoly blue (20). Small amounts of phosphorus have also been determined indirectly by polarography (21) and by atomic absorption (15, 22).

In the method described in this paper, phosphate is converted to 12-molybdophosphoric acid which is then extracted into isobutyl acetate, as recommended by Paul (23). After evaporation of the organic solvent the complex is dissolved in alkaline solution, and after acidification molybdenum(VI) is reduced to molybdenum(III). The resulting molybdenum(III) is reoxidized with iron(III) to molybdate and the resulting iron(II) is determined as iron(II) ferrozine complex. In this manner submicroamounts of phosphate have been determined by measuring the absorbance of the iron(II) ferrozine complex.

EXPERIMENTAL SECTION

Apparatus. A Cary 14 (Varian Instrument Group, Palo Alto, CA) spectrophotometer was used for all spectrophotometric measurements. The pH of solutions was determined by using an Orion (Orion Research Inc., Cambridge MA) Model 12 pH meter. Small amounts of reagents were weighted with a semimicrobalance.

Reagents. All chemicals were either analytical or primary standard grade and were used without further purification. Deionized water was used to make all solutions.

Glassware. All glassware was washed with 6 M hydrochloric acid and rinsed with deionized water.

Preparation of Standard Solutions. Stock standard phosphate solution was prepared by dissolving 0.1000 g of oven-dried analytical reagent grade disodium hydrogen phosphate, Na_2HPO_4, in 100 mL of deionized water and was stored in a