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A PHOTOMETRIC TIN DETECTOR FOR GAS CHROMATOGRAPHY

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SUMMARY

The presence of organotins in the environment appears to become a future public concern and, consequently, pose problems for the trace analyst. Since gas chromatography is capable of separating volatile tin compounds, a gas chromatographic detector selective for tin was developed. It is based on a modified Shimadzu flame photometric detector operating without wavelength discrimination. Tin compounds can be detected in amounts below 10^{-12} g and temperature programming can still be used at this sub-picogram level. Organotins respond approximately 100 to 1000 times stronger than phosphorus- and/or sulfur-containing compounds, and approximately 10,000 to 100,000 times stronger than hydrocarbons.

INTRODUCTION

Organotin compounds have been produced in very large amounts—estimate for 1975: 25,000 tons¹—for a wide variety of uses. They serve, to name but a few, as polymerization catalysts and stabilizers in the polyvinyl chloride industry, as fungicides in agriculture, and as antifouling agents in the marine environment^{1,2}.

Compared with other organometallics, *e.g.* some of the mercurials and arsenicals they are replacing, tin compounds are considered relatively innocuous and have aroused little public concern; excepting, perhaps, the “Stalino” affair of 1954, when about one hundred people died in France². Although occasional poisonings still occur from careless use of, for example, marine paints containing bis(tributyltin)-oxide, the fact that the metal will eventually end up in a harmless form—in contrast to residues containing mercury or arsenic—has done much to promote the use of organotins, and will presumably lead to an even wider usage in the future.

Some concern has been expressed about the leaking of tin-containing polymer stabilizers into food or medical infusions², and about the general presence of organotins in the environment. Better analytical methods for organotins have been a concern of WHO and IUPAC committees for some time. A recently announced \$800,000 Batelle/EPA study includes organotins in a list of ten toxic substances (among cadmium, mercury, lead, C_2HCl_3 , arylphosphates, etc.), whose effect on human physiology and the environment will be scrutinized³. Organotins are on a “black

list" (as opposed to a "grey list") of substances to be eliminated from the Mediterranean⁴.

If all of this signals the advent of world-wide monitoring for organotins—similar to efforts directed at chlorinated hydrocarbons—then analytical methods for tin compounds are in definite need of improvement. Although several good approaches exist for the determination of total tin (or even of particular tin compounds) at the formulation or field application level, a true trace method for separation and determination of various organotin species is not yet available. Thus there exists, for instance, little if any information on the potential presence of organotins in seafood.

Analytical methods for tin compounds have been well reviewed⁵. A cross-section of studies from recent years can be found in refs. 6–13 and literature listed therein. The last three papers^{11–13} describe gas chromatographic approaches.

The lack of a suitable gas chromatographic (GC) trace method for organotins—in analogy to electron-capture GC for chlorinated hydrocarbons—is most likely due to the lack of (a) a derivatization procedure suited for trace levels of common organotins and their metabolites and (b) an easily available, sensitive and selective tin detector. Tetraalkyltins have been used as derivatives due to their excellent GC properties since 1965 (see literature in ref. 13), but their suitability for trace analysis remains to be demonstrated. The search for a sensitive gas chromatographic tin detector, on the other hand, is dealt with in this paper.

As would be the case with most organometallics, a promising analytical approach is atomic spectroscopy. Tin is a rather peculiar metal in this regard—see, for instance, Gilbert's classical account¹⁴—and several features of its various emissions remain unclear as of today. A flame coupled with a gas chromatograph was described by Zado and Juvet¹⁵. It responded to a variety of metals including tin: Tin tetrachloride showed detection limits of 7×10^{-9} moles (at 358 nm) and 2×10^{-9} moles (non-selective range 355 to 625 nm).

Flames typical of atomic spectroscopy differ considerably, in size, structure, energy and environment, from those used in a typical GC detector, e.g. the flame ionization detector (FID) or the Brody and Chaney design¹⁶ of a flame photometric detector (FPD). It was the interest of our groups for some years to use these puny flames characteristic of GC detectors in single or multiple channel operation for the detection of organometallics. Generally this approach involved the monitoring of molecular bands rather than of atomic lines, because of the much lower flame energy.

The first attempt concerned an optical channel tagged onto a regular FID for tin vs. carbon detection¹⁷. Several organic tin compounds responded well at ca. 485 nm, with minimum detectable amounts of about 10 ng. (The origin of the very diffuse emission peaking at 485 is in doubt¹⁴; it has at times been attributed to SnO¹⁸.)

As a sequence to these experiments, a flame ionization detector was developed¹⁹, whose hydrogenrich atmosphere, when doped with silane, allowed us to determine unusually low amounts of various organometallics, among these compounds of tin. As little as 20 pg of tetraethyltin could be detected, with a discrimination against tetradecane of 16,000 (ref. 20).

While these results were obtained from an ionization response, the emission response of tin compounds continued to be of interest to us. With a detector better suited to the detection of low levels of light (a filterless version of the Brody-Chaney FPD), a comparable minimum detectable limit of 30 pg of tetraethyltin was found²¹.

No effort had been made at that time to optimize photometric tin response since compounds of a variety of metals were all to be tested at the same conditions. The present study was therefore designed to investigate the parameters related to tin response, to improve detector performance, and to establish analytical utility.

EXPERIMENTAL

A Shimadzu dual-channel FPD was obtained on loan, courtesy of Aminco/Shimadzu, and used with a Shimadzu 4B gas chromatograph housing a 1000×2.7 mm I.D. borosilicate column packed with 5% OV-101 on Chromosorb W, 45–60 mesh, with an injection port temperature of 250° and a detector base temperature of 250° for isothermal or 300° for temperature-programmed runs. This FPD is constructed for use with sulfur and phosphorus compounds and the response of such compounds, at optimized conditions including a Spectrum electronic filter, was checked for purposes of comparison.

The interference filters were then removed. One channel was always operated without filter, using in effect the whole range of the photomultiplier (300 to 650 nm, maximum 440 nm, S-11 response, Hamamatsu R268, Sb-Cs, borosilicate glass). The other channel served a variety of purposes, carrying at times interference filters, cut-off filters, masks, or, on occasion, a (separately supported) Jarrel-Ash 0.25-m grating spectrometer. An exhaust tube was situated above the detector to remove undesirable effluents.

Optimization of tin response

Tetraalkyltins were used as standards to optimize hydrogen and air flows to the FPD, *i.e.* to determine the maximum signal-to-noise ratio. The position of this maximum was checked and flows were re-adjusted if necessary, after each change in detector conditions.

A variety of substances were introduced into the detector either with the carrier gas (nitrogen) through the column, or via the hydrogen supply line. These included SiH_4 (in hydrogen) and CH_4 (in nitrogen) on a continuous basis, and "Silyl 8" (a silanizing mixture for column deactivation) and tetramethylsilane as large injections of neat material.

The quartz tube containing the flame gases in the Shimadzu FPD was replaced by a variety of differently shaped quartz tubes. The only ones important in the context of this paper had a constricted middle section, as shown in Fig. 2. Peak asymmetry induced by the detector was determined for a series of these tubes in isothermal runs, using tetrapropyltin as a standard.

Possible adverse effects

The influence of methane present *during* detection of an organotin standard, was investigated by adding methane to the carrier gas via a Nupro fine metering valve. The influence of a number of compounds containing phosphorus or sulphur on the response of an organotin standard eluting at a *later* time, was investigated by an appropriate sequence of injections. The consequences of injecting *large* amounts of tin compounds, on both response and peak shape of *later*-eluting tin compounds, was similarly evaluated.

Detector performance

Once the best overall conditions for detector operation were decided upon, calibration curves were run in temperature-programmed mode with five standard tin compounds, increasing and then again decreasing the injected amounts; and in isothermal mode (but at otherwise similar conditions) with typical aromatics, aliphatics, and sulfur-, phosphorus-, and sulfur-plus-phosphorus-containing compounds.

RESULTS AND DISCUSSION

The Shimadzu FPD performed significantly better than the earlier-used standard FPD²¹ in our hands, but no thorough comparison of the two detector types was carried out. Fig. 1 shows the peak resulting from 100 pg of a standard sulfur compound run at optimized conditions with and without the use of an interference filter.

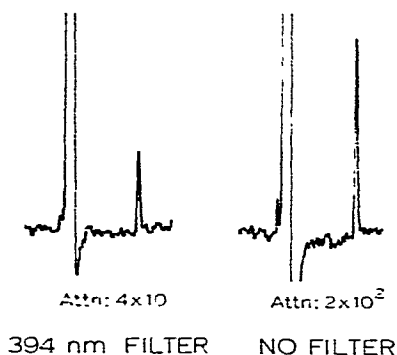


Fig. 1. Temperature-programmed chromatography, with and without 394-nm interference filter, of 100 pg of di(*tert.*-butyl)disulfide. Flow-rates in ml/min: nitrogen, 40; hydrogen, 40; air, 25. Spectrum low-bandpass electronic filter set at 0.01 Hz.

After flow-rates were optimized for tin response, a variety of interference filters, cut-off filters and masks were tested for analytical use. However, the "open mode" (no filter, no mask) provided the best overall performance. Increases in selectivity could be obtained by, for instance, using the SnH band at 610 nm; but only at the cost of a large drop in sensitivity. (We measured a bit less than 100 pg as minimum detectable amount for tetrapropyltin using a 610 nm interference filter; a drop of more than two orders of magnitude in sensitivity. However, if extreme sensitivity is not required, use of the sharp SnH band with interference and/or cut-off filter and a red-sensitive photomultiplier tube may be the better choice for a variety of analytical problems than the "open" technique pursued in this study.) The spectra that originate from tin compounds under FPD conditions are interesting subjects of study in their own right, but this spectroscopic aspect will be dealt with at another time. The following paragraphs, except where noted, pertain to tin response obtained in an "open" mode.

Two annoying features of this response became immediately apparent: Sensitivity was influenced by the FPD's history and so was the shape of the peaks. They tailed badly; an effect caused by the detector and not by the column. (Excepted

here are peaks resulting from the red emission at 610 nm, which are closer to symmetrical.)

The introduction of silicon-containing compounds to the detector increased both response and peak broadening considerably, and the effect lasted for some time after the silicon source was shut off. Tin emissions were quite sensitive to the geometry of the FPD quartz enclosure, and response as well as peak shape could change drastically when the quartz tube was altered. It was also found that injections of fluorine-containing compounds, such as are commonly used to remove silica deposits from detectors, improved response considerably. In further experiments, the detector was therefore treated periodically in this manner, and the use of silane or other silicon-containing dopants was discontinued.

Fig. 2 shows peak tailing as influenced by the inner diameter of the quartz tube above the flame. A tube similar to the one shown in cross section, with an inner diameter of 3 mm, was therefore used for all further experiments. It gave reproducibly good peak shapes and increased response for tin compounds, while discriminating against other FPD-active species. No further improvements in detector performance were attempted.

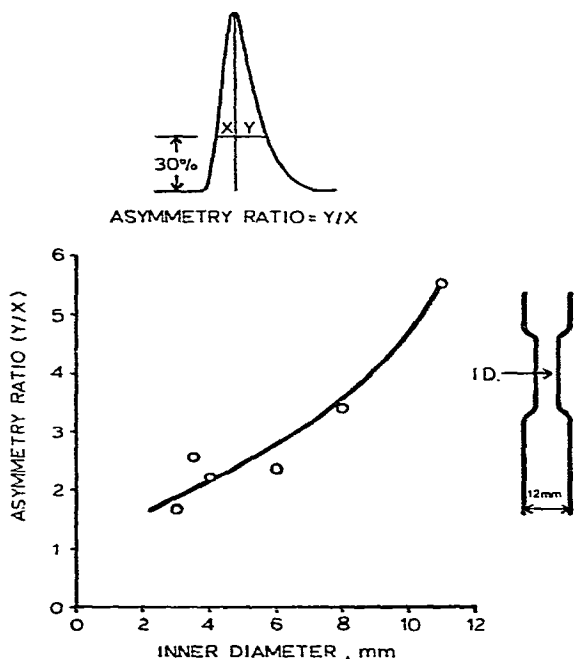


Fig. 2. Measurement of peak asymmetry of tetrapropyltin, chromatographed isothermally at 120°, correlated to the inner diameter of the quartz tube. No interference filter. Flow-rates in ml/min: nitrogen, 40; hydrogen, 250; air, 30. 100 × 0.27 cm I.D. borosilicate column, packed with 5% OV-101 on Chromosorb W, 45-60 mesh.

However, some potential interferences needed to be checked. It is well known, for instance, that some FPD responses, notably those of sulfur, are depressed by co-eluting carbon compounds. Since the detector can be "cleaned" by injections of organofluorines, substances must exist that "contaminate" it.

Into the latter category belong two types: The injection of large amounts of phosphorus-containing compounds, as well as the introduction of large amounts of tin compounds themselves, depressed the response of later-eluting organotins. This detector "poisoning" is illustrated in Fig. 3 for the case of tributyl phosphate.

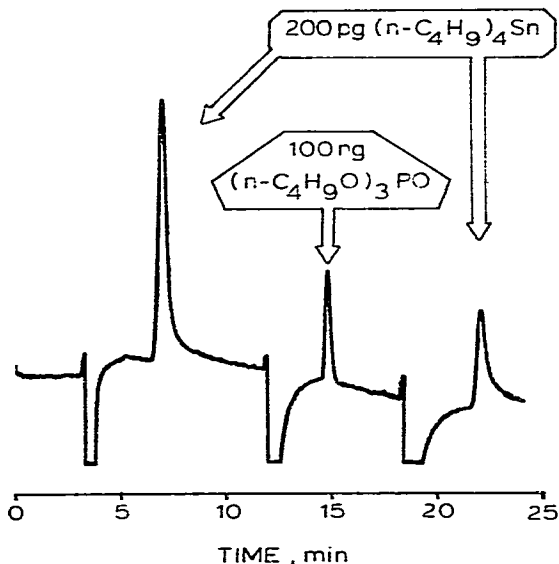


Fig. 3. Detector poisoning. Explanation in text. Conditions as in Fig. 2. Quartz tube 3 mm I.D. as shown in Fig. 2.

The effects of tin compounds are less severe—amounts beyond the linear range have to be injected to bring about response degradation and, as with phosphates, good detector performance can be restored by injection of fluoro compounds.

The effect of a co-eluting carbon compound on tin response was investigated by methane being continuously added to the carrier gas. Fig. 4 shows the results of this experiment, which included a sulfur compound (at conditions optimized for tin) in more than a thousand-fold excess for comparison. While it is obvious that tin response is depressed by co-eluting methane and the peak shape drastically altered, the amounts of methane required to produce a substantial decrease are quite large, *i.e.* more than 10% by volume of the carrier gas.

Thus, the interferences were not considered serious enough to warrant special efforts toward their circumvention. The general performance of the detector in terms of sensitivity and selectivity was therefore tested and the results are illustrated by the calibration curves shown in Fig. 5. This figure appears overlaid and, perhaps, confusing, but it seems to us to present a fairer approach to a discussion of selectivity than the common use of simple selectivity ratios. Even then, it should be realized that these curves represent only one particular detector functioning under certain obvious and not-so-obvious conditions (*e.g.* the amount of column bleed, past usage, etc.).

To characterize the relative sensitivity of two elements by a single number requires that measurements are made within the linear range for both and that, more

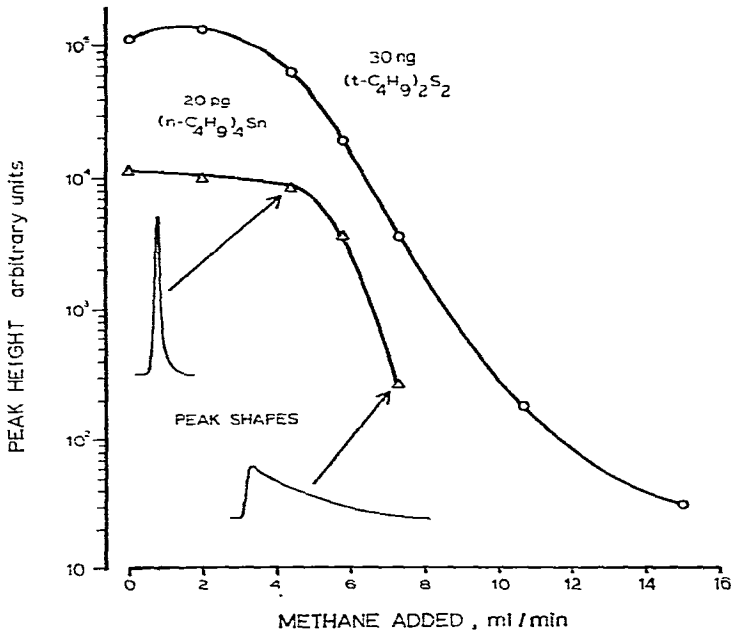


Fig. 4. Methane-doped detector. Methane flow as indicated, 3 mm I.D. quartz tube and other conditions as in Fig. 2.

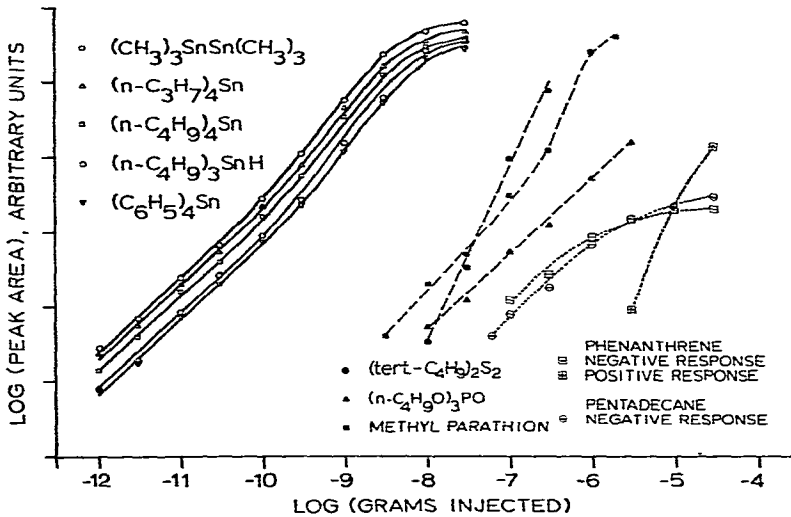


Fig. 5. Calibration curves of various standard compounds. Tin compounds: temperature program as shown in Fig. 6. Other compounds isothermal: $(tert-C_4H_9)_2S_2$, 90°; $(n-C_4H_9O)_3PO$, 160°; methyl parathion, 175°; phenanthrene, 165°; pentadecane, 140°. Other conditions and 3 mm I.D. quartz tube as in Fig. 2.

important, the responses for each element are due only to, and directly proportional to, the respective amounts of the elements introduced. If the calibration curves are non-linear or if response depends on structure, calibration curves of standard compounds convey a more accurate picture. Even so, the choice of chromatographic conditions for the elution of a compound with an exponential response (*e.g.* sulfur) will influence the results, since a sharp peak will yield higher values than a broad one. Moreover, the magnitude of the exponent, as is the case for sulfur, may vary with conditions.

The conditions used in Fig. 5 are those of optimum tin response. The organotins were runs in temperature-programmed mode, the other compounds isothermal. The phosphates were chromatographed at the end of the test in order to avoid any depression of detector performance. The following, general comments can be made.

The response of tin compounds is precisely linear over more than two decades and its magnitude, though not strictly proportional to tin content (possibly because of experimental conditions), follows approximately the correct sequence [*i.e.* $(\text{CH}_3)_6\text{Sn}_2 > (\text{C}_3\text{H}_7)_4\text{Sn} > (\text{C}_4\text{H}_9)_4\text{Sn}$, etc.]. Above this range, it becomes slightly exponential (*i.e.* a slope somewhat larger than 1 on the log-log plot), although the effect is not very pronounced. At the top of the tin calibration curves the detector obviously becomes saturated and, although the peak area measurement seems to indicate otherwise, the peak heights of all five compounds become the same. Injections much beyond this amount will cause the detector to lose sensitivity.

The pure sulfur and phosphorus compounds show their expected exponential and linear behavior; methyl parathion, which contains both elements, shows both types of behavior in the upper and lower parts of its calibration curve, respectively. Stated very roughly, the detector is two to three orders of magnitude more sensitive to tin compounds than to sulfur or phosphorus compounds, although values outside this range can be easily found.

The selectivity of tin vs. carbon compounds must be couched in equally ambiguous terms. The calibration curves suggest that the detector is more sensitive to tin compounds than to carbon compounds by four to five orders of magnitude. However, the erratic response of hydrocarbons in FPDs is well known, and a change in the nature or level of the background emission would lead to rather large changes at least in the negative peaks (*i.e.* reductions in background). Different organic structures can show different behavior; demonstrated by comparing pentadecane, whose response is negative, to phenanthrene, whose response is negative as well as positive—the former dominating at low, the latter at high amounts. Obviously, conditions can be changed to change this behavior.

It should also be remembered that these calibration curves were run without wavelength discrimination (excepting the spectral response of the photomultiplier tube), and under conditions of optimal tin response (*i.e.* at the maximum of the tin signal-to-noise profile) rather than under conditions of maximum discrimination against one or the other species. The latter approach would most likely have led to significantly different results.

On the whole, the performance of this photometric tin detector is well suited for trace analysis, as can be seen from a comparison of minimum detectable amounts reported in the literature for boron-, chromium-, sulfur- and phosphorus-containing compounds—each, of course, under its own optimized conditions and in a particular

instrument. Slowinski and Suffet²² detected 10^{-9} g decaborane, Burgett and Green²³ 10^{-11} g chromium(III)trifluoroacetylacetonate. The minimum detectable amounts listed for typical sulfur and phosphorus compounds are generally in the 10^{-9} to 10^{-11} g region. Tetrapropyltin, on the other hand, could be detected in 2×10^{-13} g amounts under the conditions described in this paper. Fig. 6 illustrates the situation by a temperature-programmed chromatography of a five-compound standard mixture, at the ten and one picogram levels. From it it appears that the GC detection problem of organotins has been solved.

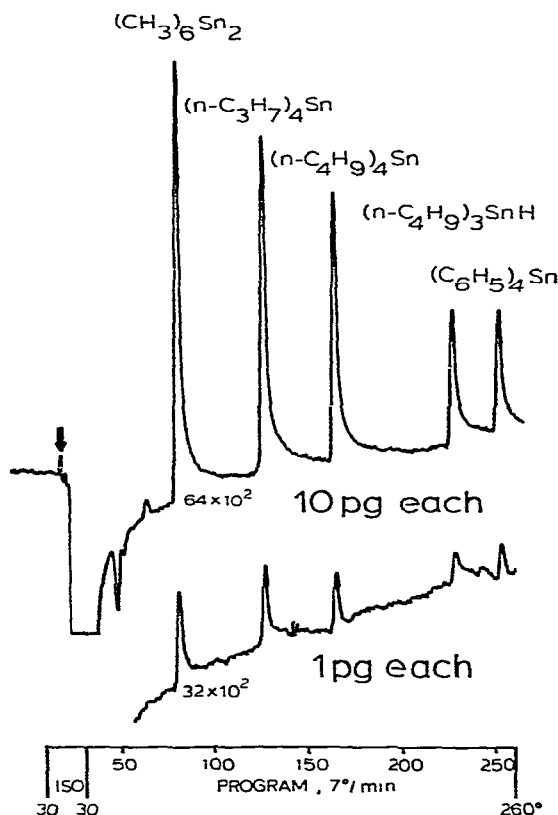


Fig. 6. Temperature-programmed chromatographies of a standard mixture. Other conditions and 3 mm I.D. quartz tube as in Fig. 2.

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