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A tin-sensitive hydrogen flame detector*

Organic tin compounds find widespread application as polymer stabilizers, fungicides, insecticides, organic catalysts, oil additives, etc.[1]. Among the various approaches used for their analysis, gas chromatography (GC) has proven one of the most versatile[2]. In this case, the thermal conductivity cell or, less frequently, the hydrogen flame provide non-selective detection.

There has also been some interest in selective detection of tin compounds after separation by gas–liquid chromatography (GLC)[3-6], but results have not been too encouraging.

The problem approached in this study was how to provide to the highly sensitive, but essentially non-selective, hydrogen flame ionization detector (FID) a second channel with selectivity for tin. One of the obvious possibilities for devising a complementary detector mode is to monitor the optical emission of tin. Of course, flame photometry is a common method for elemental tin determinations[7]; however, no hook-up with GC has been reported, and the hydrogen or nitrous oxide flames used in photometric procedures differ greatly from the puny flame of an FID used in GC. Flame photometric detectors (FPD) for GLC effluents have been reported for various other atomic or molecular species (see, *inter alia*, refs. 8–11). In a few cases, both the electrical conductivity and the optical emission of a hydrogen flame were monitored[8,12-14].

We decided to use the basic design described by our laboratory for a "dual-mode indium flame detector"[15] in conjunction with a half-meter Ebert spectrometer.

The goal of our investigation was essentially to preserve the high sensitivity and reliability of the FID — which implies the use of a small flame and restricted ranges of flow rates — and to define the tin response obtainable from a photometric channel under these circumstances. It would have been unreasonable to expect the optimum flow rates to be similar for the electrical (carbon) and optical (tin) modes; however, we hoped to find some range of conditions suitable for both of them.

Experimental

The GC and electronic hardware was the same as described in ref. 14. Fig. 1 shows a detector cross-section with the Jarrell-Ash 82-000 spectrometer attached. For an initial scanning of the tin spectrum — provided by tetramethyltin introduced continuously into the flame by a slow flow of nitrogen — two slits of 250-μ width were used. In actual chromatography, though, both slits were removed and the width of the light-path was limited only by the slit assembly — an operational mode akin to using 3-mm slits. The spectrometer was held in position by two labjacks sitting on a table; however, a better solution may have been to affix the detector to the spectrometer and connect the former to the gas chromatograph via a heated capillary.

The detector was kept gas-tight by gaskets cut from silicone rubber sheets. This feature bears little significance for tin compounds, but served to reassure the

analyst when more toxic metal organics were chromatographed — in which case the detector outlet was connected to suitable scrubber tubes.

Photometric response profiles were measured for tetramethyltin at 485 nm, varying the nitrogen, hydrogen, and air supplies. These profiles suggested the following optimal flows in ml/min: N_2, 45; H_2, 90; air, 335.
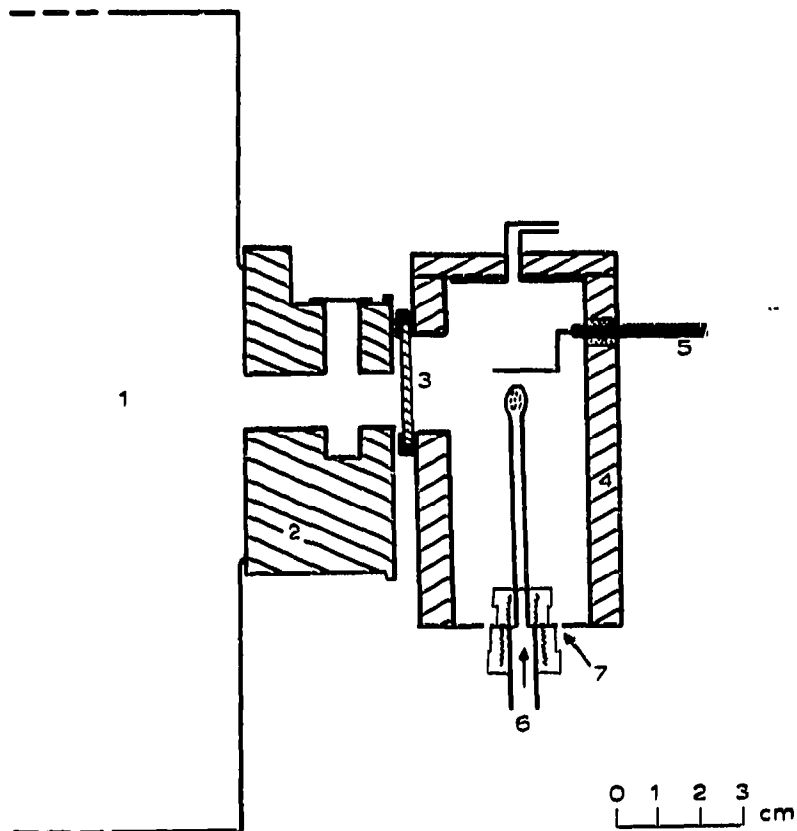

Fig. 1. Detector assembly. (1) Jarrell-Ash 0.5-m Ebert scanning spectrometer, (2) Jarrell-Ash Model 82-015 slit assembly without slits, (3) quartz window, (4) aluminum detector housing, (5) collector electrode assembly, (6) GC column, (7) air inlet.

Under these conditions, then, calibration curves were established for peak areas of tetramethyltin, trimethyltin chloride, tetraethyltin, and tetra-n-butyltin.

A 2 m × 4 mm I.D. Pyrex U-tube column was packed with 3 % OV-101 on AW Chromosorb W, 80–100 mesh. Using a ballistic temperature program from 30 to 186°, solutions containing equimolar amounts of the tin compounds (together with a 50-fold molar excess of n-dodecane) were chromatographed and detected simultaneously on both channels.

Results and discussion

Fig. 2 shows the calibration curves for the model tin compounds on the photometric channel; they are linear from ca. $10-10^4$ ng injected. Phototube noise is responsible for the lower limit.

Fig. 3 shows chromatograms simultaneously recorded on both channels. The flow conditions chosen are optimal for photometric tin; had the conditions been optimized for ionizable carbon (*i.e.* H_2, ca. 60 ml/min; N_2 and air, as before), the
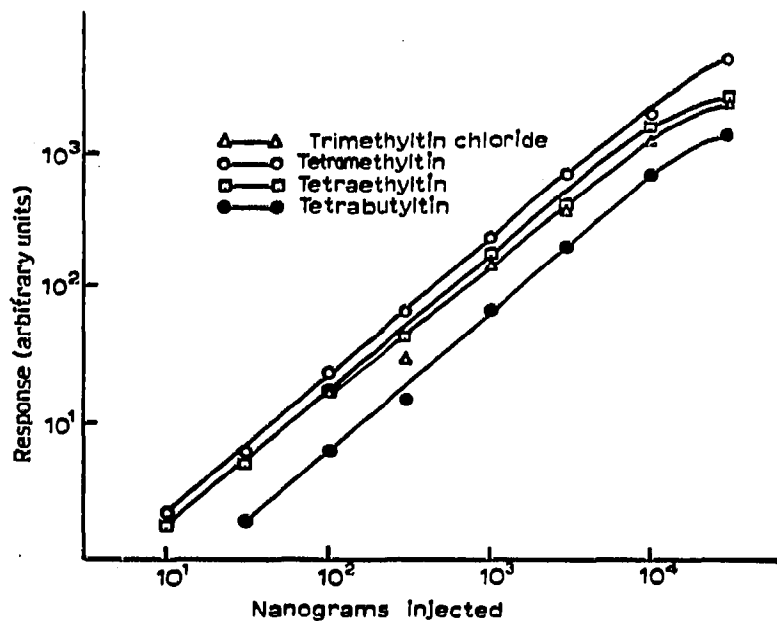
Fig. 2. Response profiles of tin compounds. Column: 3% OV-101 on 80–100 mesh AW Chromosorb W, 2 m × 4 mm I.D. Pyrex; flow rates (ml/min): $N_2 = 45$, $H_2 = 90$, air = 335; wavelength monitored: 485 nm; oven temperatures: tetramethyltin at 30°, trimethyltin chloride at 70°, tetraethyltin at 115°, and tetra-n-butyltin at 188°.
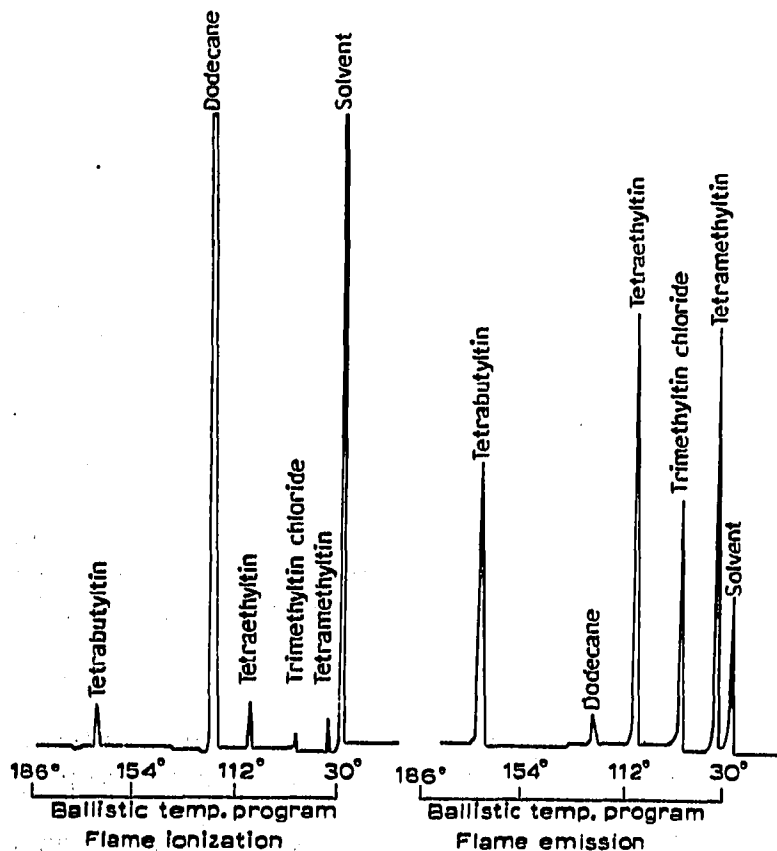

Fig. 3. Simultaneous flame ionization and flame emission responses of a mixture containing dodecane and various tin compounds (in 50:1 molar ratios) in diethyl ether.

tin response would have declined and the carbon response risen by about half of their respective values.

As could be expected from the different percentages of tin in the model compounds, the response on an equal-weight basis increases in the order of tetra-*n*-butyltin, trimethyltin chloride, tetraethyltin, and tetramethyltin. Yet, the response of tiimethyltin chloride seems lower than would be predicted on a weight basis alone. No effort was made, however, to establish whether this effect was of structural origin or due to decomposition of trimethyltin chloride on the GC column.

The wavelength chosen is one of several which can conceivably be used. Operating with apparent slit-widths of 3 mm obviously means trading selectivity for sensitivity. The photometric channel thus approaches the sensitivity of an FID for tin compounds, but discriminates against other compounds only by a factor of about 400. If higher selectivity is called for, suitably smaller slits can be used, at a corresponding sacrifice in the lower limit of detection.

The most important parameter in the optimization of the detector is the hydrogen flow, and the respective values of 60 and 90 ml/min for the FID and FPD responses are close enough to allow efficient two-channel operation. Since the photometric signal was considered the "weaker" one of the two, Figs. 2 and 3 were obtained at conditions optimized for tin response. However, the proper choice of hydrogen flow, as well as the choice of slit-width, is a matter to be decided on the requirements of each particular type of analysis.

Proper choice of spectrometer settings and detector gas flows, furthermore, allows the described flame unit to be used not only for volatile tin compounds, but for other organometallics as well.

Department of Agricultural Chemistry,   WALTER A. AUE
University of Missouri,   HERBERT H. HILL, JR.
Columbia, Mo. 65201 (U.S.A.)

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