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Short communication

Analysis of organotin compounds by gas chromatography–reactive-flow detection

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Abstract

The gas chromatographic (GC) reactive-flow detector (RFD) responds strongly to organotin compounds. The system yields over four orders of linearity with a minimum detectable amount of $8 \cdot 10^{-16}$ g Sn/s (at $S/N = 2$). The RFD's selectivity towards tin over carbon is approximately $2.5 \cdot 10^5$ g C/g Sn. The spectral emission includes a surface luminescence centered at 390 nm and a gas-phase luminescence centered at 470 nm. These findings suggest that the GC–RFD could serve as a sensitive and selective tool for the analysis of organotin compounds. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Reactive-flow detection; Detection, GC; Organotin compounds

1. Introduction

The determination of organotin compounds in the environment is an important analytical procedure due to the variable toxicity these pollutants possess according to their chemical structure [1–3]. Selective detection has been employed in the chromatographic determination of organotin compounds for many years (e.g., Refs. [4–7]). Gas chromatography (GC) with a flame photometric detector (FPD) has been widely used for this purpose due to the detector's rugged, inexpensive design, and the possibility of

choosing either the red SnH emission or the more sensitive tin luminescence on a quartz surface (e.g., Refs. [8–12]).

Recently, we developed a novel GC detector, dubbed 'reactive-flow detector' (RFD), which monitors the chemiluminescence generated by a low-temperature (as low as 200°C) reacting column of pre-mixed hydrogen and air [13]. In addition to sharing certain elemental response characteristics with the FPD, reactive-flow detection also offers benefits of its own. For instance, when current is measured in the air-rich flame atop the luminescent column, the RFD delivers an electrical response comparable to that of the flame ionization detector (FID), which is different in nature ('orthogonal') to the photometric signal produced inside the capillary [14]. Furthermore, the RFD is not susceptible to response quenching in the presence of hydrocarbons, a process that has caused significant problems for the

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FPD [15,16]. During the course of investigating these features, the RFD was observed to produce a strong response for several elements including tin. The present paper describes the examination of tin response in the RFD, with the aim of optimizing this new source of chemiluminescence for the analysis of organostannanes.

2. Experimental

A detailed description of the RFD is available [13]. The detector is constructed on the base of an old Tracor Model 550 FID system. The RFD system creates a stable, luminescent gas column (~35 mm in length) by the low-temperature reaction of a fuel-rich hydrogen–air pre-mixture that flows, together with the column effluent, through a quartz or borosilicate glass capillary (35 mm × 1.8 mm I.D.). On top of the capillary, a separate, external supply of air maintains a steadily burning air-rich flame. The emission is sampled midway down the capillary via a glass image conduit (6 in. × 0.25 in. O.D.; 1 in. = 2.54 cm; No. 38307, Edmund Scientific, Barrington, NJ, USA) that guides the light to a photomultiplier tube (R-268 or R-374 with wavelength ranges of 300–650 nm and 185–850 nm, respectively; Hamamatsu, Bridgewater, NJ, USA). For the recording of spectra, a quartz rod and a 0.25 m Jarrell–Ash monochromator (1180 lines/mm grating, 3.2 nm/mm bandpass) are substituted for the above-mentioned combination of image conduit plus photomultiplier, and the wavelength drive is advanced manually after each replicate injection of analyte.

A borosilicate column (2 m × 1.8 mm I.D.) packed with 10% Apiezon L on Chromosorb W (45–60 mesh, about 350–250 μm average particle diameter) performs the separations. (Note: a packed column was used for convenience and because the ancient gas chromatograph did not support a capillary column, which would have given better performance. To account for this, detectabilities will be given in minimum detectable *flows*, i.e. in g Sn/s or mol Sn/s. These figures of merit should be equally applicable to packed and capillary columns.) Typical gas flows are 12 mL/min nitrogen through the column, 40 mL/min hydrogen and 60 mL/min air through the reactive-flow capillary, and 150 mL/min

air through the detector housing to support the upper flame. Variations used for optimizing response are discussed below.

3. Results and discussion

Initial efforts explored the RFD's response to tin by monitoring those gas supply ranges that create a 'reactive flow'. Fig. 1 plots the signal-to-noise (S/N) ratio produced by the chromatographic peak of an organotin compound against the air flow through the capillary. The numbers aside each data point represent the supply of hydrogen (in mL/min) that conveniently establishes a stable reactive flow for each particular air setting. As can be seen, the lowest possible gas flows yield an S/N response 'maximum' that rapidly decreases as the flow settings increase. The maximum correlates with the optimal RFD gas flows found earlier for sulfur- and phosphorus-containing compounds [13]. However, the decline in tin response is more rapid, possibly owing to the chemistry of its light emission, or to a slight stoichiometric variation between the two settings, or both.

Of more interest, though, is the emergence of a second tin response maximum (yielding about the same S/N value) at a much higher pre-mix flow-rate, a phenomenon that has never before been observed. It seems unique to tin amongst all the elements that, so far, are known to respond in the RFD. Analysis of the data shows the appearance of this second maximum to be due to an increase in signal rather than a decrease in noise. Further, as the gas flows increase and reactive flow is maintained, the pre-mixture becomes disproportionately richer in hydrogen. If a common chemiluminescent excitation mechanism exists for most RFD spectra — as has been suggested for the FPD [16] — then the second RFD maximum may be associated with a different species or a different mode of tin luminescence becoming dominant. Earlier studies indicated that the background luminescence of the RFD was occasionally reduced by injection of an organolead compound, whose passage through the detector was visually observed to remove 'hot spots' from the glass surface [13]. This background emission often increased considerably at higher gas flows, a phenom-

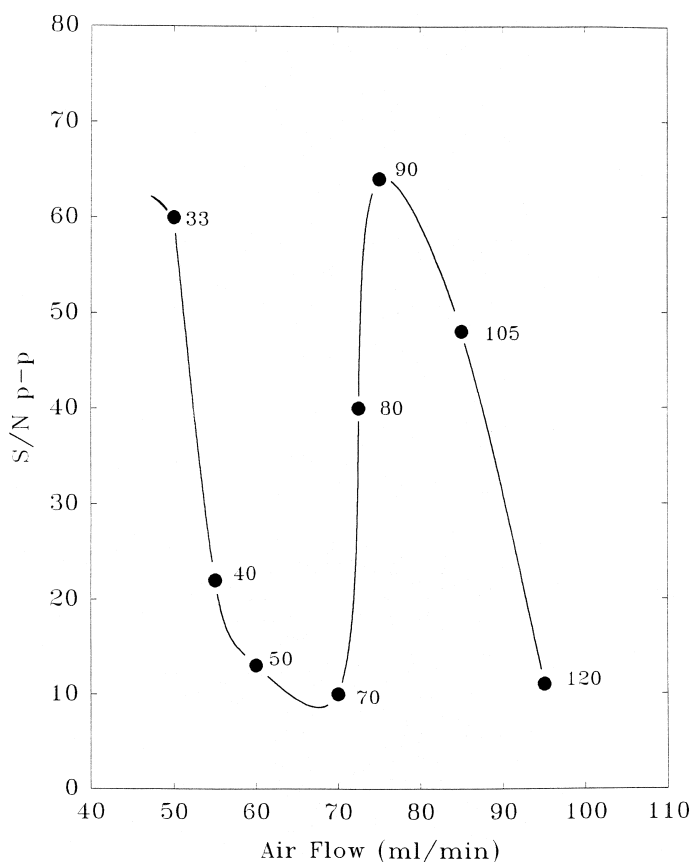


Fig. 1. RFD tin response given as signal over peak-to-peak baseline noise (S/N_{p-p}) for various pre-mix air settings (mL/min) that yield a reactive flow. The pre-mix hydrogen flow (mL/min) is given alongside each data point. Tin was injected into the GC–RFD system as 2 pg tetrabutyltin.

enon that may have been related to a more ‘active’ capillary surface. To better understand the nature of RFD tin emission and to address the presence of the second maximum in Fig. 1, emission spectra were recorded for the three most interesting reactive-flow conditions.

Fig. 2 displays the RFD tin emission spectra taken at flow settings corresponding to the one minimum and the two maxima in Fig. 1. Two main features exist under all three conditions: a blue emission centered near 390 nm, and a greenish emission centered near 470 nm. As the gas flows increase, the spectral contribution at 470 nm changes but little. At the same time, however, the emission at 390 nm increases from moderate at low flows to dominant at high flows. The two spectral features are similar to

those found for tin chemiluminescence in the FPD. The green spectrum likely originates from SnOH^* ; the origin of the blue spectrum is unknown but could possibly be related to SnO^* [10]. Visually, these respective emissions are observed in the RFD as a greenish-grey gas-phase luminescence present throughout the capillary volume, and a blue emission emanating from the capillary surface. (Incidentally, when μg or larger quantities of organotins are injected into the GC–RFD, the red SnH^* emission becomes noticeable around 610 nm.)

Considering its spectral and visual appearance, the second maximum observed in Fig. 1 is clearly the result of an increased tin surface luminescence on the walls of the capillary. This may be the result of an increased H_2 content producing a higher H^{\cdot} radical

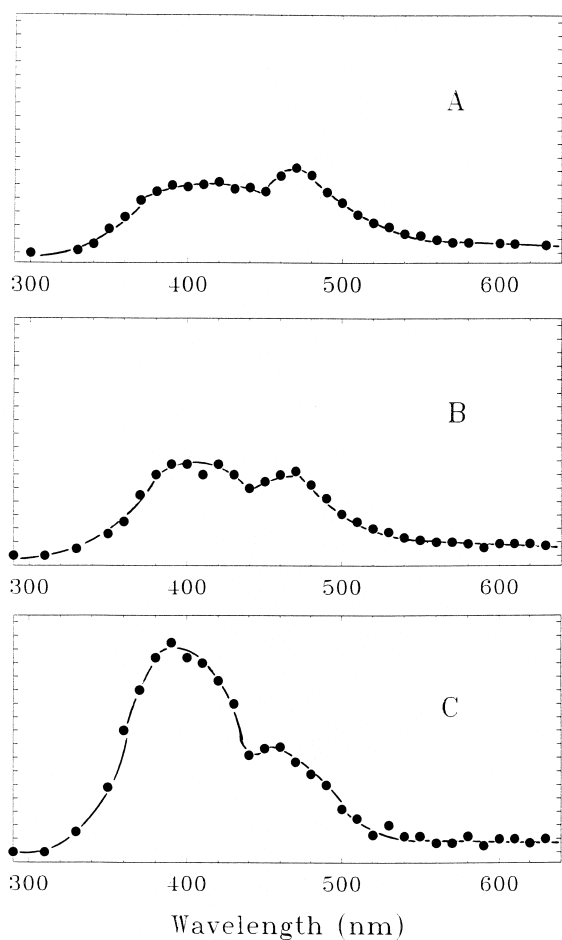


Fig. 2. Tin emission spectra recorded at various settings from Fig. 1. RFD gas flows (mL/min) are: (A) 33 H₂ and 50 air; (B) 70 H₂ and 70 air; and (C) 90 H₂ and 75 air. Bandpass, 30 nm. R-374 photomultiplier tube.

recombination rate on or close to the silicic surface. Hydrogen recombination is believed to energize much of the chemiluminescence observed in the FPD [17]. While the three spectra — blue, green and red — appear to be the same in RFD and FPD, their relative intensities clearly differ. In the RFD, the blue and green spectra are of very high and somewhat comparable intensity, while the red spectrum is much weaker. In the conventional FPD, the blue spectrum is of much higher intensity than the roughly comparable green and red spectra. There are other differences between RFD and FPD as well. The FPD, at least in our hands, displayed the blue tin

luminescence on a (clean) quartz surface, but not on borosilicate glass. Furthermore, the FPD quartz surface was easily ‘poisoned’ [10]. These phenomena depended somewhat on detector conditions (cf. Refs. [8,12]). In case of the RFD, however, borosilicate glass works as well as quartz in terms of light emission (although quartz is preferred for transmitting the UV part of the blue spectrum). Furthermore, in the RFD the blue spectrum appears even on silicic surfaces that had previously been exposed to larger amounts of lead, phosphorus or, for that matter, tin compounds (cf. Ref. [10]).

Although both maxima in Fig. 1 produce the same approximate *S/N* value, the higher gas flow is found to cause a stronger background emission and occasional fluctuations in the reactive flow. Hence, for general operating conditions, the low-flow maximum (i.e. the one found with a pre-mix of ca. 33 mL/min H₂ and 50 mL/min air) was chosen as the preferred setting. Yet, under different analytical circumstances — perhaps in the context of selectivity vis-à-vis other elements — use of the high-flow maximum may still become the option of choice.

Fig. 3 displays a typical organotin calibration curve as obtained under optimal RFD conditions. The line in the figure is purposely drawn at a slope of precisely 1, and it ends just at the *S/N* value of 2. Noise here is measured as the peak-to-peak fluctuation of the baseline, with spikes and drift excluded. As observed from Fig. 3, RFD exhibits a linear organotin response spanning over four orders of magnitude. The RFD detection limit for tin is determined from this curve to be $8 \cdot 10^{-16}$ g/s, as illustrated by the inset chromatographic peak originating from 1 pg tetrabutyltin. Hydrocarbon response under the same conditions was found previously to be $2 \cdot 10^{-10}$ gC/s [13]; this indicates that the RFD should have a selectivity of greater than five orders of magnitude for tin over carbon. Experimentally (and without an optical filter) it was found that 100 ng of dodecane was needed to produce the same response as 1 pg of tetrabutyltin. This corresponds to a selectivity of $\sim 2.5 \cdot 10^5$ g C/g Sn.

4. Conclusions

The RFD response of tin has been investigated and

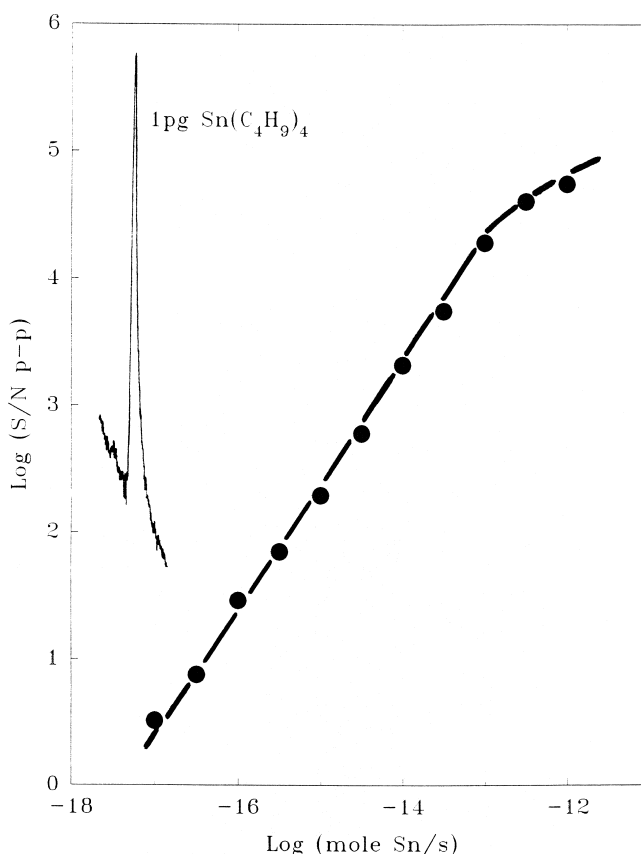


Fig. 3. GC–RFD response (S/N_{p-p}) for different amounts of tin (mol Sn/s). The line is drawn at an exact slope of 1. Inset: chromatographic peak from a 1 pg injection of tetrabutyltin.

the results indicate that the GC–RFD could become a sensitive and selective tool for the analysis of organotin compounds, at either one of two distinct response maxima. The tin emission under both reactive-flow conditions results from the combination of a surface luminescence centered at 390 nm and a gas-phase luminescence centered at 470 nm, with the former most prevalent at high flows, the latter most obvious at low flows. These findings confirm that the analytical utility of the RFD extends beyond the initially investigated elements of sulfur and phosphorus, with excellent figures of merit obtainable for organotins. While the RFD displays many similarities to the FPD, it also exhibits distinct and important differences. Differences of a general nature are the auxiliary FID-like response to carbon and the welcome absence of hydrocarbon quenching; differences

of a nature peculiar to tin are the accessibility of two response maxima (at two distinctly different reactive-flow regimes) and the relative freedom from surface-poisoning effects. Similar to the FPD, the RFD may become analytically valuable not only for organotins but also for volatile compounds of other elements.

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