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Note

Phosphorus response in a hydrogen-atmosphere flame ionization detector for gas chromatography

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Universal acceptance of silylation techniques as pre-chromatographic treatments for many polar and non-volatile compounds has prompted a search for silicon-selective detectors. Perhaps the most promising, practical and selective detector for silicon compounds results from a simple modification of a standard flame ionization detector (FID) to produce a hydrogen-atmosphere flame ionization detector (HAFID)¹. In this detector a unique flame suppresses ionization of normal hydrocarbons while retaining the sensitivity of a standard FID for silicon-containing compounds. During studies comparing responses of carbon and silicon compounds using a wide variety of flame conditions, it was found that under certain operating conditions responses for both silicon and carbon compounds were positive^{2,3} whereas under others, carbon compounds produced positive responses and silicon-containing compounds produced negative responses⁴. By switching between the two operating conditions, which requires only minor adjustments in detector-gas flow-rates, complicated and time-consuming sample-cleanup may be eliminated and silicon-containing compounds can be easily identified in complex sample matrices⁵.

Although earlier HAFID studies focused on Si/C response characteristics of the flame, it was noted that other heteroatom-containing compounds often produced responses dissimilar to those from compounds containing only carbon and hydrogen⁴. Some of the most analytically significant responses observed were those for phosphorus compounds. This paper describes the basic response characteristics of phosphorus compounds in this HAFID.

EXPERIMENTAL

Experiments and chromatograms described in this paper were performed on a Hewlett-Packard 5710a gas chromatograph using a 10 m × 0.2 mm I.D. methylsilicone-coated fused-silica capillary column (Hewlett-Packard, Avondale, PA, U.S.A.). Flow-rates used throughout these studies were as follows: helium carrier gas, 1.2 ml/min; helium make-up gas, 40 ml/min. For isothermal operation the column oven temperature was held at 90°C, 150°C, and 170°C during studies with chloroben-

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zene, ferrocene, and triethylphosphate, respectively. For temperature-programmed operation, the oven was heated from 70°C to 150°C at 8°C/min.

The HAFID was constructed atop the Hewlett-Packard instrument and was identical in design to the silicon-selective detector reported in ref. 4. Detector-gas flow-rates were as follows: hydrogen, 1600 ml/min; oxygen, 130 ml/min. Ferrocene-saturated nitrogen gas was premixed with hydrogen at various rates to produce the desired concentration of doping agent in the detector atmosphere. A schematic diagram of the doping apparatus can be found in ref. 3. Gas flow-rates for the FID, a standard Hewlett-Packard unit, were maintained at 30 ml/min for hydrogen and 240 ml/min for air, as recommended by the manufacturer.

The primary test compounds were ferrocene (Aldrich, Milwaukee, WI, U.S.A.), chlorobenzene, and triethylphosphate (Chem. Service, West Chester, PA, U.S.A.). Each was diluted in glass-distilled hexane (Burdick & Jackson Labs., Muskegon, MI, U.S.A.) to the desired concentration. Other test compounds were *n*-octanol, *n*-decanol (Chem. Service), decane, dodecane, and tetradecane (Sigma, St. Louis, MO, U.S.A.).

Response from repetitive injections of 320 ng of ferrocene, triethylphosphate, and chlorobenzene were monitored as a function of the concentration of ferrocene

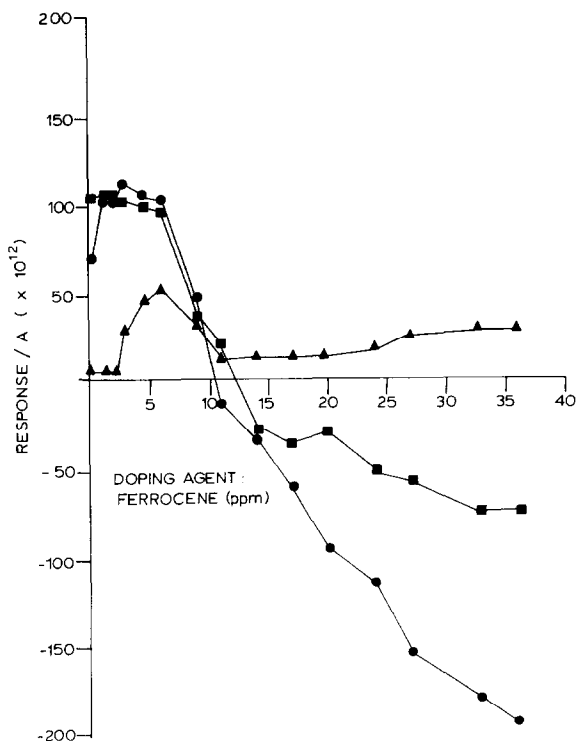


Fig. 1. Response dependence on doping concentration. Peak-height responses of triethylphosphate (●), ferrocene (■) and chlorobenzene (▲) are plotted as a function of ferrocene concentration in the hydrogen atmosphere of the detector.

vapor in the hydrogen atmosphere. Calibration curves were determined at an electrode height of 110 nm by a series of injections of ferrocene, triethylphosphate, chlorobenzene when the detector was not doped with ferrocene and when the detector was doped with 5 ppm and 30 ppm of ferrocene. Positive and negative responses of the HAFID were compared to FID responses for a mixture of test compounds.

RESULTS AND DISCUSSION

Like silicon-containing compounds, phosphorus compounds were found to be sensitive to changes in the concentration of the ferrocene. Triethylphosphate increased in sensitivity by *ca.* 50% when the hydrogen gas was doped with a small amount (*ca.* 5 ppm) of ferrocene (Fig. 1). However, response rapidly decreased at higher doping concentrations up to *ca.* 10 ppm, where the direction of the chromatographic response was reversed. At concentrations greater than 10 ppm, response for phosphorus compounds became more negative with increased doping up to the limit that the experimental apparatus could supply. At the maximum doping level allowable, 45 ppm, the phosphate standard exhibited a negative response that was *ca.* 3 times more intense than the positive response it produced when no doping agent was present. This pattern of enhanced positive responses at low ferrocene doping levels and negative responses at higher doping levels is similar to that observed for silicon-containing compounds. This response behavior was also observed when the doping agent, ferrocene, was injected into the chromatograph as a test compound. Other compounds containing heteroatoms such as oxygen, nitrogen, or halogens have not been found to produce negative responses.

Responses for halogenated compounds, such as chlorobenzene, were also found to be altered by the introduction of the dopant. However, negative responses were not observed. Chlorobenzene sensitivity reached a maximum value, at 7 ppm ferrocene, of *ca.* 10 times its non-doped response and leveled off, at higher doping concentrations, to a response that was only 3–5 times that of its non-doped response.

Fig. 2 illustrates these results with chromatograms of a mixture of various test compounds. In the FID tracing, chromatogram a, all nine test compounds are detected as expected. Chromatogram b, in which the HAFID was doped with 5 ppm of ferrocene vapor, provides peaks for only four of the nine compounds—a small positive peak for the hexane solvent and enhanced positive peaks for chlorobenzene, triethylphosphate and ferrocene. No traces of the other compounds in the mixture are observed. Chromatogram c, in which the HAFID was doped with 30 ppm of ferrocene vapor, shows a positive peak for the hydrocarbon solvent and chlorobenzene along with pronounced negative peaks for triethylphosphate and ferrocene. For the purpose of this discussion, “positive-doped mode” refers to those HAFID conditions used to obtain chromatogram b and “negative-doped mode” refers to those conditions used to obtain chromatogram c.

For both of these detection modes, responses for the primary test compounds were found to be linear over about three orders of magnitude down to their detection limits. The only exception was ferrocene in the negative-doped mode, where the slope of the calibration curve on a log–log plot proved to be less than one, indicating that at this high level of doping, the flame had become saturated with ferrocene. Repetitive injections of standards at the same concentration were as reproducible in the HAFID

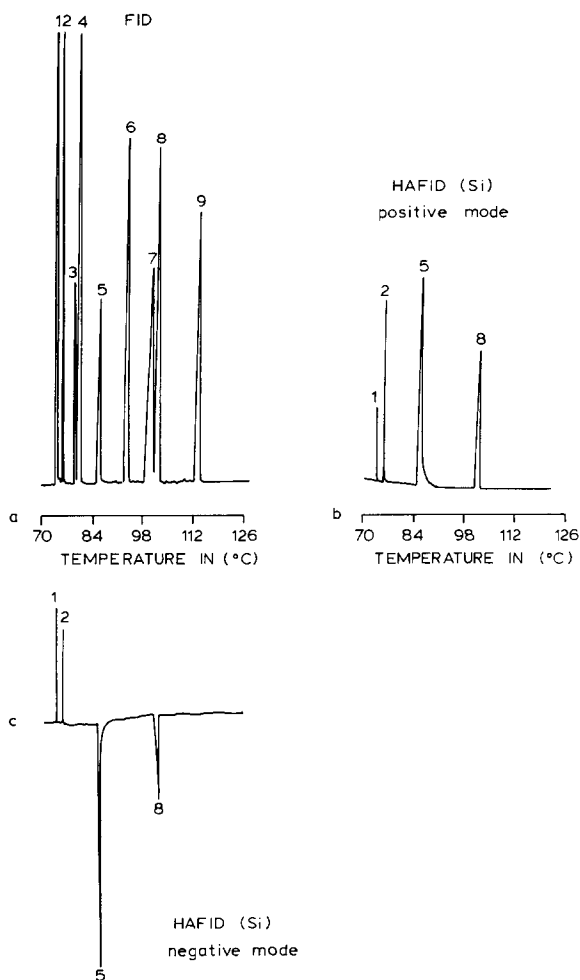


Fig. 2. Example chromatograms using different detection methods. A standard mixture of equal amounts of chlorobenzene, decane, octanol, triethylphosphate, dodecane, decanol, ferrocene, and tetradecane in hexane as solvent was separated under identical chromatographic conditions using different methods of detection. Chromatogram a was obtained with a standard FID; chromatogram b with a HAFID that had been doped with 5 ppm of ferrocene; and chromatogram c with a HAFID that had been doped with 30 ppm of ferrocene. Peaks: 1 = hexane; 2 = chlorobenzene; 3 = decane; 4 = octanol; 5 = triethylphosphate; 6 = dodecane; 7 = decanol; 8 = ferrocene; 9 = tetradecane.

as in the FID. Reproducibility was limited only by the injection technique.

Minimum detectable amounts, based on double the peak-to-peak noise level, are listed in Table I. Note from Fig. 1 that the most sensitive response for the phosphate standard is achieved in the negative mode whereas Table I shows that the lowest amount detectable is achieved in the positive mode. In the negative mode, the minimum amount detectable was limited by a two-fold increase in noise due to the addition of relatively large quantities of the doping agent. The flame peak-to-peak

TABLE I
MINIMUM DETECTABLE AMOUNTS

HAFID mode of operation	Compounds containing			
	Silicon	Phosphorus	Iron	Chlorine
Non-doped	4 ng*	7 ng	0.6 ng	50 ng
Positive-doped	50 pg**	0.5 ng	1 ng	2.5 ng
Negative-doped	1 ng***	1 ng	14 ng	9 ng

* Data obtained from ref. 2.

** Data obtained from ref. 3.

*** Data obtained from ref. 4.

noise level for the non-doped and positive-doped mode was $ca. 1.5 \times 10^{-13}$ A whereas flame noise in the negative-doped mode was $ca. 3 \cdot 10^{-13}$ A.

Although phosphorus-sensitive detectors such as the nitrogen-phosphorus ionization detector or the flame photometric detector, are commercially available, the HAFID may prove useful in situations where these detectors are not available in laboratories and an inexpensive method for the selective detection of phosphorus compounds after gas chromatography is needed. It can be relatively easily constructed from a standard FID and, as long as the doping agent is maintained at the proper level, it provides a reproducible and linear response that can be employed for quantitative analysis.

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