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SURVEY OF SELECTED HYDRIDES AS DOPING AGENTS FOR A HYDROGEN-ATMOSPHERE FLAME-IONIZATION DETECTOR

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SUMMARY

The hydrogen-atmosphere flame-ionization detector for gas chromatography exhibits a selective and enhanced response for metal containing compounds when its atmosphere is doped with small amounts of silane. In this study, response characteristics of the flame were investigated for a variety of organic compounds when the hydrogen atmosphere was doped with small amounts of methane, silane, germane, or phosphine. Responses of pure hydrocarbons and compounds containing F, Cl, O, S, N, P, As, Sb, Si, or Ge were either unaffected by the addition of doping agents, or their variations were not considered analytically significant. As expected, compounds of Fe, Sn and Pb exhibited enhanced responses with silane doping. Mo and W compounds showed increased ionization with methane. Several compounds increased response with the introduction of germane, but noise also increased such that no gain in signal-to-noise ratio was obtained.

Phosphine proved to be the doping agent with the most potential. Response intensities for compounds containing Fe, Sn, Pb, Mo and Sb appeared analytically useful, but more significant, was the fact that the peaks were negative. Thus, it appears that a potential exists for the development of a phosphine-doped detector in which compounds not containing elements of interest would produce diminutive positive peaks while metal containing compounds would respond with enhanced negative peaks. Further studies on this mode of operation are recommended.

INTRODUCTION

When properly optimized, a hydrogen-atmosphere flame-ionization detector (HAFID), constructed from a commercial flame-ionization detector (FID), is capable of detecting sub-picogram quantities of certain metal compounds with selectivities against hydrocarbons greater than 10^5 (ref. 1). Direct gas chromatographic (GC) determinations of antiknock agents, tetraethyllead and methylcyclopentadienylmanganese, in gasolines have recently been demonstrated².

Operation of an HAFID differs from that of an FID in that the oxident (air, enriched with oxygen) is introduced to the flame with carrier gas while the fuel (hydrogen, doped with small amounts of silane) is brought directly into the detector

to produce a reducing atmosphere. While position, potential and polarity of the collector electrode, flow-rates of detector gases, and general geometry of the detector housing have been shown to affect response^{1,3,4}, enhancement of metal ionization by addition of silane to the hydrogen atmosphere is the detector's most mechanistically interesting requisite.

Silane may be involved with charge transfer processes that enable ions produced from burning metal compounds to be more efficiently collected by the electrode¹, but its function is not well understood. Since silane is the only doping agent that has ever been investigated, a survey of several hydrides as dopants for the hydrogen atmosphere was undertaken to compare their effect on response. This paper reports the results of that survey.

EXPERIMENTAL

Conditions

An FID on a Hewlett-Packard 5830A gas chromatograph was converted to an HAFID as described in ref. 2. This detector was maintained at 250°C throughout this study with gas flows of 1600 ml/min for hydrogen, 120 ml/min for air, 150 ml/min for oxygen and 20 ml/min for the helium carrier gas. A 6 ft. × 1/4 in. O.D. (2 mm I.D.) borosilicate column packed with 80–100 mesh Ultra-bond 20 M (RFR, Hope, RI, U.S.A.) was used with oven temperatures selected for individual test compounds to achieve practical retention times. Once an operating temperature was established, each compound was chromatographed at that temperature throughout the study. The injection port was maintained at 225°C.

Procedures

Test compounds used in this study are listed below along with their supply sources. Fluorobenzene, chlorobenzene, dipropylsulfide and amyl ether (Eastman Organic Chemicals, San Francisco, CA, U.S.A.); hexacarbonyltungsten, hexacarbonylmolybdenum and tetrabutylgermane (Alfa Division, Ventron, Danvers, MA, U.S.A.); ethyl benzene and pyridine (Fisher Scientific, Santa Clara, CA, U.S.A.); tetraethylsilane (Pfaltz & Bauer, Stanford, CT, U.S.A.); dodecane (Alitech, Arlington Heights, IL, U.S.A.); tetraethyllead (ICN Pharmaceuticals, Plainview, NY, U.S.A.); ferrocene, tetrabutyltin, triphenylantimony and triphenylarsine (Aldrich, Milwaukee, WI, U.S.A.); nitrobenzene and tributylphosphate (J. T. Baker, Hayward, CA, U.S.A.); and aniline (Mallinkrodt, St. Louis, MO, U.S.A.).

Each compound was selected for its structure or type of heteroatom it contained. Individual solutions in "glass-distilled" hexane (Burdick & Jackson Labs., Muskegon, MI, U.S.A.) were prepared at concentrations ranging from $1 \cdot 10^{-10}$ g/ μ l to $1 \cdot 10^{-6}$ g/ μ l in decade steps. A 0.5- μ l volume of solution was injected at the concentration required to produce a measurable peak at $1 \cdot 10^{-10}$ A f.s. These signals, which were substantially above noise level for all experimental conditions, allowed comparison of concentrations with approximately equal responses. Reproducibility was always better than 10%.

Methane, silane, germane, and phosphine, obtained from Airco Specialty Gases (Santa Clara, CA, U.S.A.) as 1% CH₄ in hydrogen, 100 ppm SiH₄ in hydrogen, 1% GeH₄ in hydrogen and 1% PH₃ in hydrogen, were investigated as doping agents.

Each hydride was added to the hydrogen atmosphere at a mixing ratio of approximately 10 or 50 ppm. The condition in which no doping agent was added to the hydrogen atmosphere was also investigated.

Responses of the different test compounds for each doping condition were compared by calculating the ionization ratio (ϵ), the number of ions responding/number of molecules of test compound injected. These ratios were calculated from the relation

$$\epsilon = R/MF$$

where R is response in Coulombs, M is moles of test compound injected and F is Faraday's constant. Results are reported as $-\log \epsilon$ or, by analogy with p -functions as $p\epsilon$.

To insure against errors from unwarranted contaminations, responses for each test compound were established in a non-doped system prior to the addition of doping agents. Moreover, responses using the lower mixing ratio (10 ppm) were always obtained before those using the higher mixing ratio (50 ppm). Between the addition of each doping agent, the detector was cleaned by washing with HCl, rinsing with distilled water and acetone, and baking at 300°C overnight. Non-doped responses were confirmed with ferrocene and dodecane to insure that effects of previous doping agents had been eliminated before experiments with the next doping agent were begun.

RESULTS AND DISCUSSION

Table I lists results obtained for flame ionization of each of nineteen test compounds under nine doping conditions. Data are reported as the negative log of the ionization ratio ($p\epsilon$). A parenthetically enclosed minus sign following a $p\epsilon$ value denotes that the chromatographic peak was observed as a decrease in the flame's background current (*i.e.*, as a negative peak).

An arbitrary $p\epsilon$ value of 5.00 was chosen as that below which a response for a given compound was indicative of analytical utility. The basis for selection of this cut-off value was its comparison with normal FID values. Commercial FIDs commonly respond with a sensitivity of 0.015 C/g of carbon, producing approximately one ion for each 500,000 carbon atoms introduced into the flame. For dodecane in the FID, a $p\epsilon$ value would be on the order of 4.6. Values of 5.00 indicate that test compounds have only slightly less sensitivity in the HAFID than a hydrocarbon has in an FID. Since in this study only two dopant concentrations were selected, it is probable that optimal operating conditions for the HAFID were not achieved and ionization efficiencies can be improved over those reported here.

Table II ranks test compounds whose responses qualified as analytically useful. The lowest $p\epsilon$ value observed was 2.04, obtained for ferrocene when hydrogen was doped with 50 ppm of silane. The first two peaks in Fig. 1 demonstrate that the ferrocene response is increased at least 1000 times by the addition of silane since 50 pg of the compound gave a slightly larger peak when the detector was doped with silane than did 50 ng of ferrocene without doping. Both germane- and methane-doping enhanced ferrocene response less than silane-doping.

As expected from earlier studies, tetrabutyltin and tetraethyllead also responded

TABLE I
SUMMARY OF ρ_B VALUES

Compound	ρ_B	CH_4 (10 ppm)	CH_4 (50 ppm)	SiH_4 (10 ppm)	SiH_4 (50 ppm)	PH_3 (10 ppm)	PH_3 (50 ppm)	GeH_4 (10 ppm)	GeH_4 (50 ppm)
Fluorobenzene	6.45	6.29	6.60	6.40	6.40	6.10	5.99	6.76	7.08
Hexacarbonyltungsten	4.97	4.94	4.84	5.05	4.68	6.07 (-)	5.63 (-)	5.02	5.52
Hexacarbonylmolybdenum	4.12	4.05	3.80	4.16	4.02	4.30 (-)	4.10 (-)	4.88	5.77
Dipropylaldehyde	6.86	6.69	6.85	6.77	6.26	7.12	6.49	6.63	7.24
Ethyl benzene	6.56	6.56	6.68	6.45	6.51	6.20	6.16	6.73	7.40
Tetraethylsilane	6.71	6.49	6.78	6.49	6.73	6.18	6.27	6.72	7.41 (-)
Pyridine	6.48	6.39	6.73	6.36	6.32	6.15	6.00	6.59	7.31
Chlorobenzene	6.35	6.33	6.54	6.80	6.58	6.00	5.86	6.59	6.95
Amyl ether	6.72	6.66	6.95	6.66	6.70	6.20	6.10	6.71	7.70
Dodecane	6.60	6.56	6.89	6.48	6.56	6.04	5.89	6.69	6.62
Tetraethyllead	6.44	6.28	6.15	5.48	4.47	5.64 (-)	4.56 (-)	3.80	5.47
Ferrocene	5.30	5.25	4.88	3.79	2.04	3.76 (-)	3.46 (-)	4.20	5.30
Nitrobenzene	6.34	6.33	6.71	6.29	6.27	5.86	5.87	6.30	6.35
Aniline	6.82	6.49	6.80	6.56	6.50	6.19	6.03	6.51	6.70
Tetrabutylgermane	6.36	6.22	6.59	5.32	5.02	5.02	5.30 (-)	6.11	6.64
Tetrabutyltin	5.56	5.46	5.63	4.59	3.69	4.82 (-)	4.26 (-)	3.65	5.14
Tributylphosphate	6.63	6.57	6.72	6.59	5.22 (-)	6.09	6.10	5.56	6.45
Triphenylantimony	6.54	6.48	6.72	5.72	5.30	5.92 (-)	4.62 (-)	6.21	6.41
Triphenylarsine	6.57	6.48	6.70	6.47	6.02	6.16	5.96	5.81	6.02

TABLE II
RESPONSES INDICATING ANALYTICAL POTENTIAL

<i>Compound</i>	<i>Response</i>	<i>Condition</i>
Ferrocene	2.04	SiH ₄ (50 ppm)
	3.46 (-)	PH ₃ (50 ppm)
	3.76 (-)	PH ₃ (10 ppm)
	3.79	SiH ₄ (10 ppm)
	4.20	GeH ₄ (10 ppm)
	4.88	CH ₄ (50 ppm)
Tetrabutyltin	3.65	GeH ₄ (10 ppm)
	3.69	SiH ₄ (50 ppm)
	4.26 (-)	PH ₃ (50 ppm)
	4.59	SiH ₄ (10 ppm)
	4.82 (-)	PH ₃ (10 ppm)
Tetraethyllead	3.80	GeH ₄ (10 ppm)
	4.47	SiH ₄ (50 ppm)
	4.56 (-)	PH ₃ (50 ppm)
Hexacarbonylmolybdenum	3.80	CH ₄ (50 ppm)
	4.02	SiH ₄ (50 ppm)
	4.05	CH ₄ (10 ppm)
	4.10 (-)	PH ₃ (50 ppm)
	4.12	No doping
	4.16	SiH ₄ (10 ppm)
Triphenylantimony	4.30 (-)	PH ₃ (10 ppm)
	4.88	GeH ₄ (10 ppm)
	4.62 (-)	PH ₃ (50 ppm)
Hexacarbonyltungsten	4.68	SiH ₄ (50 ppm)
	4.84	CH ₄ (50 ppm)
	4.94	CH ₄ (10 ppm)
	4.97	No doping

strongly when silane was introduced as a doping gas, but surprisingly, these compounds responded best with 10 ppm of germane. Addition of germane, however, dramatically increased noise, as can be seen in Figs. 2 and 3. Thus, signal-to-noise ratios (the primary criteria for judging analytical utility) decreased when compared to the silane doped system. Although the origin of this noise is unclear, a heavy brown deposit which coated the inside of the detector housing and the collecting electrode during germane-doping may indicate that the noise was caused by formation of particles such as Ge₃N₄ in the flame. An insulating layer of this material on the collecting electrode apparently reduced the effective electrical field and when germane-doping was increased from 10 to 50 ppm, background current and sensitivity decreased as is shown in Tables I and III. Doping with germane is not analytically useful unless these problems can be eliminated.

Hexacarbonylmolybdenum and hexacarbonyltungsten produced their most sensitive responses with methane-doping. They also exhibited the most sensitive responses of any of the test compounds when no doping agents were added to the detector. Thus, it may be possible to use the HAFID for metal carbonyls without doping the hydrogen-atmosphere.

Phosphine proved the most interesting of doping agents investigated since, when added to the hydrogen-atmosphere at the 50-ppm level, strong *negative* responses for ferrocene, tetraethyltin and tetraethyllead were observed, as is shown in Figs. 1-3.

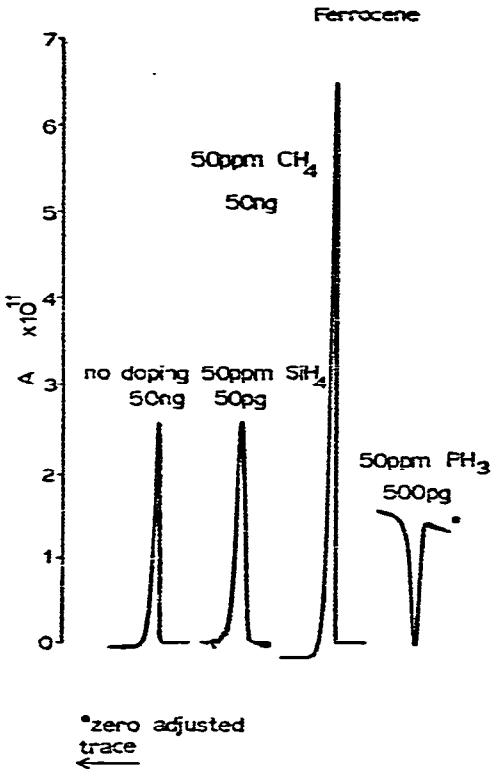


Fig. 1. Selected chromatographic peaks of ferrocene. (In all figures, recorder pen traced from right to left.)

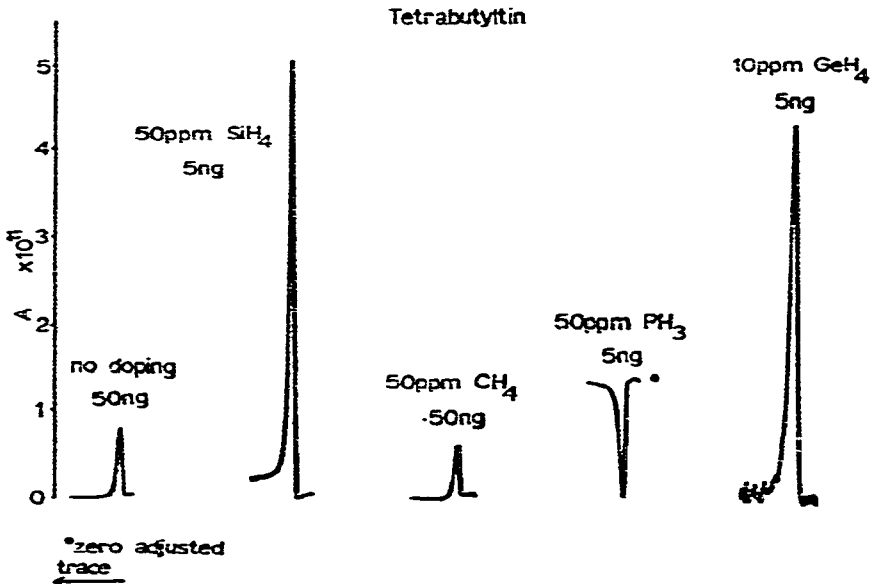


Fig. 2. Selected chromatographic peaks of tetrabutyltin.

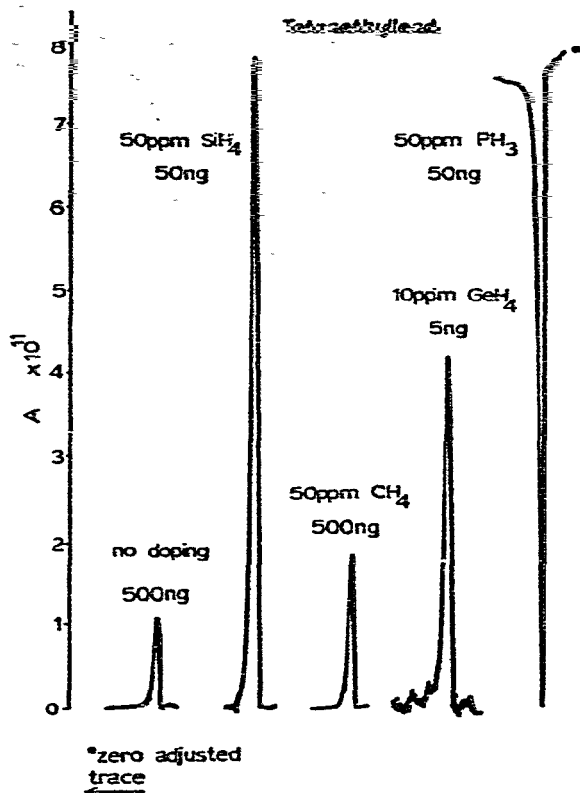


Fig. 3. Selected chromatographic peaks of tetraethyllead.

TABLE III
HAFID BACKGROUND CURRENT

Condition	Background current (nA)
No doping	0.27
CH ₄ (10 ppm)	0.35
CH ₄ (50 ppm)	0.40
SiH ₄ (10 ppm)	0.32
SiH ₄ (50 ppm)	0.36
PH ₃ (10 ppm)	0.68
PH ₃ (50 ppm)	0.82
GeH ₄ (10 ppm)	0.41
GeH ₄ (50 ppm)	0.17

Hexacarbonyltungsten, hexacarbonylmolybdenum, tetrabutylgermane and triphenylantimony also responded negatively with phosphine, while all other compounds exhibited positive peaks.

Three other test compounds, tetraethylsilane, tetrabutylgermane and tributylphosphate, showed interesting results as illustrated in Figs. 4-6. Note that each of these compounds contains a heteroelement which is contained in one of the doping hydrides. Detector responses for tetraethylsilane with silane-doping, for tetrabutyl-

germane with germane-doping, and for tributylphosphate with phosphine-doping were not significantly different from those obtained without doping. Responses for tetraethylsilane and tetrabutylgermane, Figs. 4 and 5, were unique in that they exhibited peak tailing with 10 ppm phosphine. Since this phenomenon did not occur when these compounds were detected under other doping conditions, tailing cannot be attributed to chromatography, but must be due to residual ionization in the detector after the peak has passed through the flame. When the higher amount of phosphine was introduced, the peak for tetrabutylgermane was nearly symmetrical

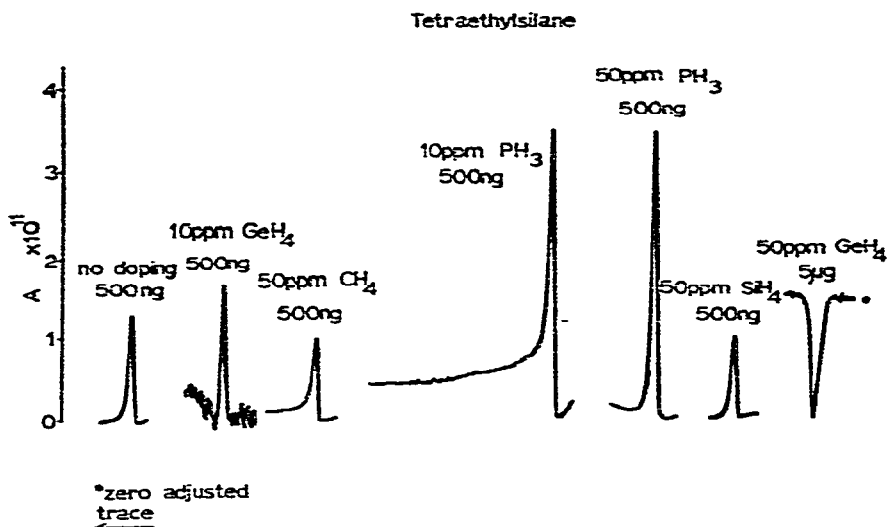


Fig. 4. Selected chromatographic peaks of tetraethylsilane.

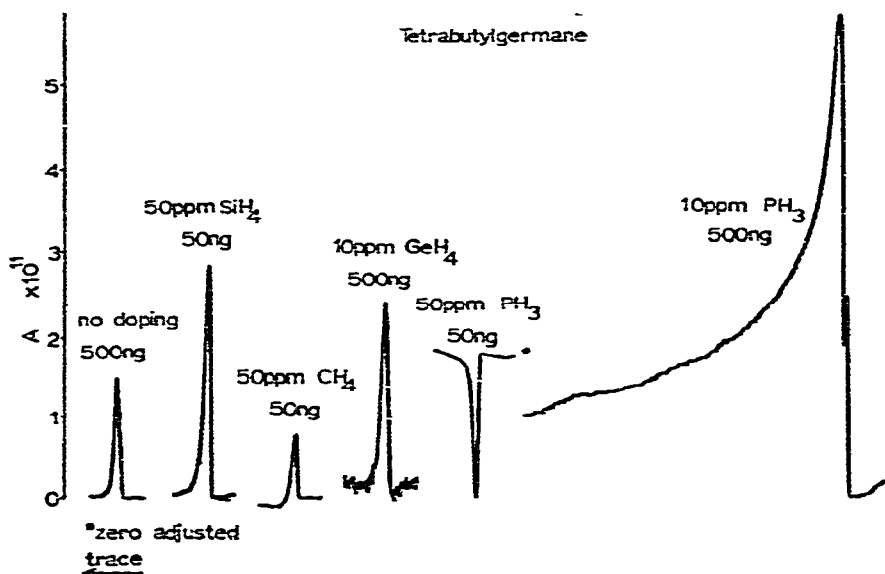


Fig. 5. Selected chromatographic peaks of tetrabutylgermane.

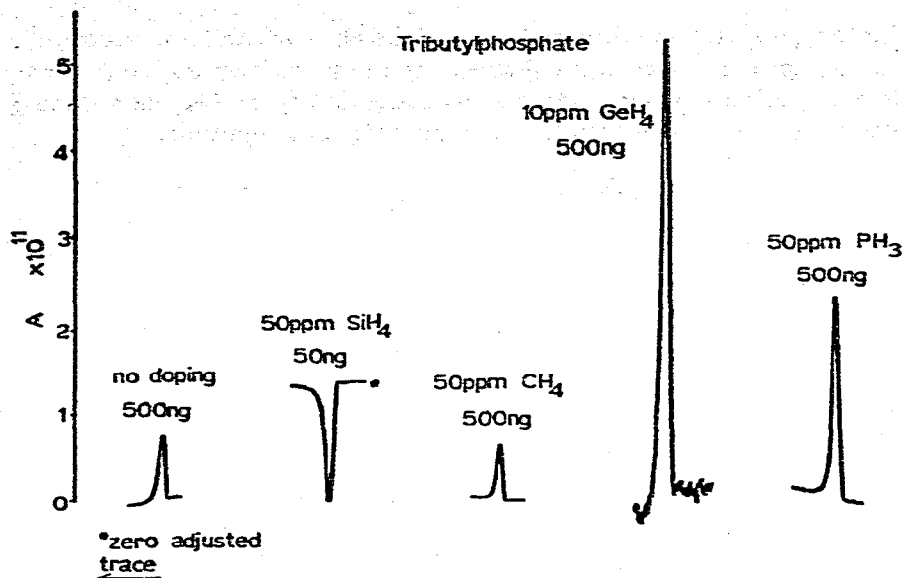


Fig. 6. Selected chromatographic peaks of tributylphosphate.

but inverted. Peak inversions as a function of doping concentration have been observed before¹ but their mechanism has not been explained. Other peak inversions in this study were also seen: the tributylphosphate peak inverted when silane was increased from 10 to 50 ppm as is shown in Fig. 6 while the tetraethylsilane peak inverted when germane was increased from 10 to 50 ppm as is shown in Fig. 4.

The occurrence of negative peaks raises the intriguing question of how responses in the HAFID are obtained. Negative responses, of course, result from a reduction in the background current of the flame. From Table III, which compares background currents at each operating condition, the background current produced with phosphine is seen to be more than three times that of the non-doped system and at least twice that of any of the other doped systems. It may be that formation of pH_4^+ in the detector is responsible for this current which can be readily neutralized when certain anions are produced during combustion of GC eluents. This explanation is, of course, speculative and incomplete. It does not explain why some compounds produce negative responses while others produce positive ones, nor does it explain peak inversions. Currently, work is underway to identify ions in a silane-doped, a phosphine-doped and a non-doped HAFID. Until ion identities are known, it is difficult to discuss mechanisms of these detectors.

In general, the remainder of the test compounds (dodecane, ethyl benzene, amyl ether, aniline, nitrobenzene, pyridine, chlorobenzene, fluorobenzene, dipropylsulfide and triphenylarsine) responded with reduced sensitivity and remarkable stability regardless of changes in doping conditions. Dodecane had a pE value of around 6.6, indicating that the HAFID response is about two orders of magnitude less than that of the FID for hydrocarbon compounds. This reduction in sensitivity can be attributed to oxidation to CO and CO_2 in the oxygen rich pre-combustion zone of the HAFID⁵ and to the relative locations of the collecting electrodes in the HAFID and the FID.

Fig. 7 shows typical responses for dodecane where all were similar in magnitude except that with 50 ppm PH_3 which was enhanced several times over the non-doping condition. This enhancement is not sufficient to reduce utility of PH_3 as a doping agent since dodecane response increased less than an order of magnitude.

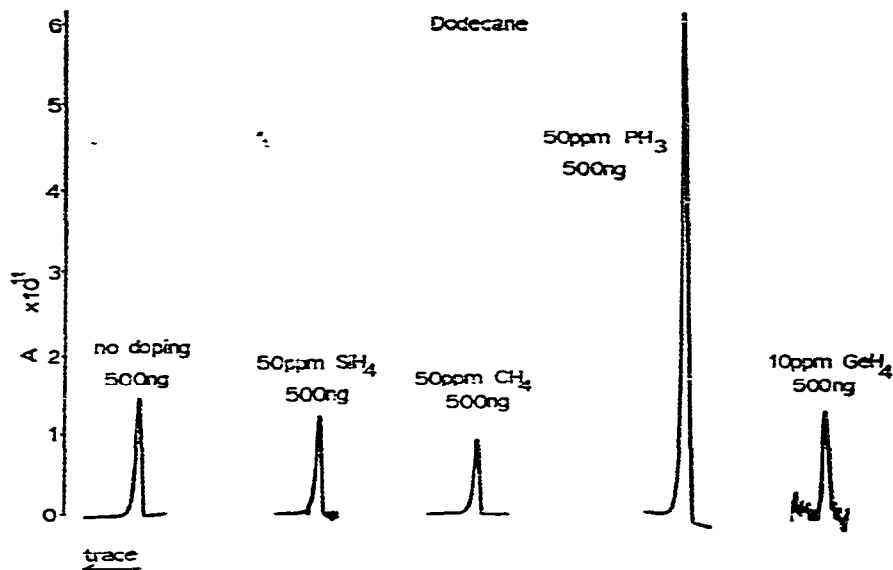


Fig. 7. Selected chromatographic peaks of dodecane.

The detector's ability to discriminate against compounds containing C, H, O, N, P, or halides (those that make up the bulk of complex organic matrixes where traces of organometallics may be contained) under a variety of doping conditions is indicative of its potential as a selective analytical tool for the analyses of metal containing compounds by GC. Although application of a phosphine-doped HAFID must be approached with caution, due to the high toxicity of this doping gas, it appears promising since response is not only sensitive and selective for metal compounds but is also specific for them by the virtue of inverted peaks.

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