DETECTION OF HETEROATOMS IN GAS–LIQUID CHROMATOGRAPHIC EFFLUENTS BY ION-EXCHANGE FLAME EXCITATION AND IONIZATION

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SUMMARY

A series of ion-exchange reactions between the effluent gases of a hydrogen flame ionization detector and crystalline salts positioned above the flame were explored as possible bases for detecting heteroatoms. Fluorine-containing compounds released chloride from calcium, barium and iron(II) chlorides for detection by alkali flame ionization. The response to sulphur was lower. Fluorine- and chlorine-containing compounds released sulphur or phosphorus from calcium sulphide or calcium hypophosphite, respectively, for detection by flame photometry. The results obtained were consistent with the idea that the high specific sensitivity of several detectors could be extended to different heteroatoms through the use of on-line ion exchange in the effluent of a hydrogen flame. The primary requirements for the salt appear to be heat stability and deliquescence, and that the cation react with the hetero-atom to form a less soluble salt and/or a more volatile acid gas.

INTRODUCTION

Several element-specific hydrogen flame detectors have been developed for gas chromatography. Various metals, phosphorus and sulphur have been detected by direct flame-excitation spectrometry[1-5]. Halogens have been detected by their reaction on the surface of a heated metal source whereby the volatility of the metal is increased; the increased concentration of the metal is then detected by flame ionization or flame emission[6,7]. Phosphorus and several other non-metals can also be detected by their effect on the degree of ionization of alkali metals in a flame[8-11].

We have previously reported the detection of fluorine in gas–liquid chromatographic effluents by a more indirect technique. Organofluorine compounds are burned in a hydrogen flame, releasing hydrogen fluoride. The flame gases are passed through a bed of calcium chloride crystals, in which fluoride is exchanged with chloride, releasing hydrogen chloride. The chloride is then detected by alkali flame ionization[12]. The sensitivity of this device to organic compounds containing fluorine and those containing chlorine demonstrated that a substantial fraction of the fluoride was exchanged during the brief period of contact between the flame gases and the crys-

tals. The use of other, similar, reactions, coupled to still other sensitive detection mechanisms, thus seemed feasible.

In the work reported here, we explored several different reactions in order to define the characteristics of the crystals, the heteroatom, the resulting product and the detection mechanism that might form the basis of sensitive and specific detection schemes.

EXPERIMENTAL

The alkali flame ionization detector (AFID) for fluorine was constructed using a Packard (Downers Grove, Ill., U.S.A.) Model 811 flame ionization detector (FID) as its base and the AFID attachment described previously[13] to detect the chlorine evolved. A 45-mesh platinum screen brazed to a stainless-steel ring served as the support for the exchange medium. The screen was positioned between the two detectors (Fig. 1).
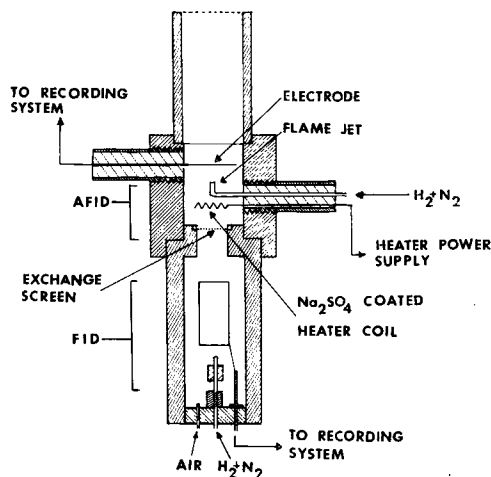

Fig. 1. Cross section of AFID fluorine exchange detector.

The photometric exchange detector was constructed using the same base and screen (Fig. 2). The flame photometric (FPD) or upper detector was similar to that described by Brody and Chaney[5] except that its base was omitted. Its flame could thus be positioned directly above and in the path of the flowing gaseous effluent of the lower flame. The light emitted was monitored with an American Instrument (Silver Spring, Md., U.S.A.) R136 photomultiplier and No. 10-268 microphotometer, using a 405-nm interference filter for monitoring for sulphur emission and a 530-nm interference filter for phosphorus emission. Both filters had a band width of 12 nm at half the transmission peak height.

In both the AFID and the FPD, the ionization current in the bottom, or flame, ionization detector was recorded simultaneously with the electrical output, either ionization current or photomultiplier tube current, of the upper flame.

The gas chromatograph was a Packard Model 802 fitted with two 180 cm × 3 mm I.D. coiled glass columns packed with 10 % ethylene glycol adipate polyester on
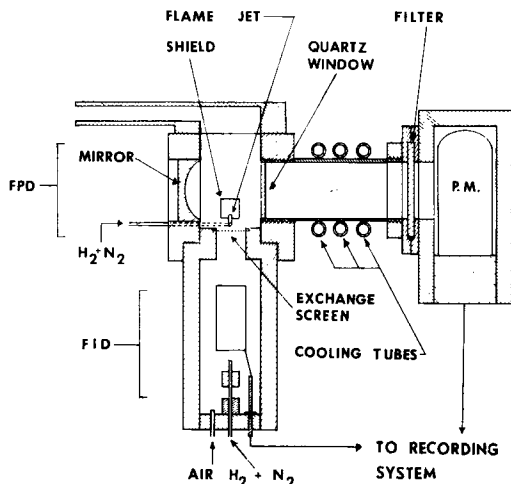
Fig. 2. Cross section of FPD fluorine exchange detector.

Chromosorb W, 80–100 mesh (Supelco, Bellefonte, Pa., U.S.A.). Two columns were operated simultaneously. The effluent of one column was fed to the flame ionization detector and that of the other to the upper flame. Test compounds could thus be introduced into either top or bottom flame in order to compare detection sensitivity. In the analysis of the test mixtures, the columns were maintained at 100° with nitrogen carrier gas flowing at 30 ml/min into both columns for the AFID work. Hydrogen was delivered to both detectors at 100 ml/min and air at 400 ml/min. In the FPD experiments, the column flow-rates were increased to 100 ml/min, the hydrogen flow-rate to the FPD to 400 ml/min, and the air flow-rate to 500 ml/min.

Barium chloride, barium hydroxide, calcium chloride, calcium sulphide, iron(II) sulphide, cobalt(II) sulphate, lithium sulphate, nickel sulphate, toluene and n-hexane were all reagent-grade materials (Fisher Scientific, Fair Lawn, N.J., U.S.A.). Chlorobenzene, trifluorotoluene, triethyl phosphate, nitropropane and fluorobenzene were obtained from Eastman Organic Chemicals, Rochester, N.Y., U.S.A. Calcium hypophosphite (anhydrous) was obtained from City Chemical Co., New York, N.Y., U.S.A. Barium sulphide was prepared from barium hydroxide by bubbling hydrogen sulphide gas into a solution of barium hydroxide and then separating the barium sulphide by fractional crystallization.

RESULTS

AFID detection of fluorine

The sensitivity of the AFID fluorine detector differed when different chloride salts were used as ion-exchange media (Fig. 3). With calcium chloride, the response to fluorobenzene was approximately half that to chlorobenzene and the response to thiophene was only slightly less. There was a minimal, non-specific response to toluene and no response to nitrobenzene. With barium·chloride, the response to fluorine was somewhat less, compared with that to chlorobenzene, indicating a lower degree of exchange. Under these conditions, there was a comparably
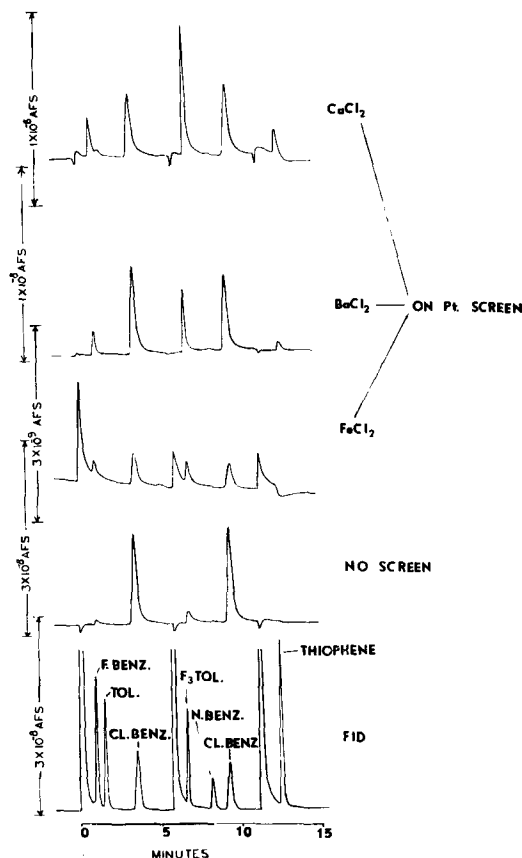
Fig. 3. Fluorine detection with different exchange media. Response of AFID exchange detector to 3.3 μg each of (left to right): fluorobenzene, toluene, chlorobenzene, (solvent) trifluorotoluene, nitropropane, chlorobenzene, (solvent) thiophene. The lowermost record is the response of the lower flame (FID). The other records, from bottom to top, are the record of the upper flame with (1) no screen, (2) FeCl$_2$, (3) BaCl$_2$ and (4) CaCl$_2$.

diminished response to thiophene and even less response to toluene and nitrobenzene. With iron(II) chloride, there was appreciable response to the n-hexane solvent front. The relative sensitivity to fluorine was similar but the overall sensitivity to chlorine was diminished. The baseline current, presumably attributable to the evolution of chloride from the screen, was least with the barium chloride.

The response of the detector to trifluorotoluene was directly proportional to the amount injected over the range 10 ng–10 μg (Fig. 4).

FPD sulphur detector for detecting fluorine

Replacement of the AFID detector for chlorine with the FPD resulted in a response to direct introduction of sulphur and phosphorus compounds into the FPD, or upper flame, that was qualitatively similar to that described by Brody and Chaney[5]. The response to thiophene increased with the square of the concentration
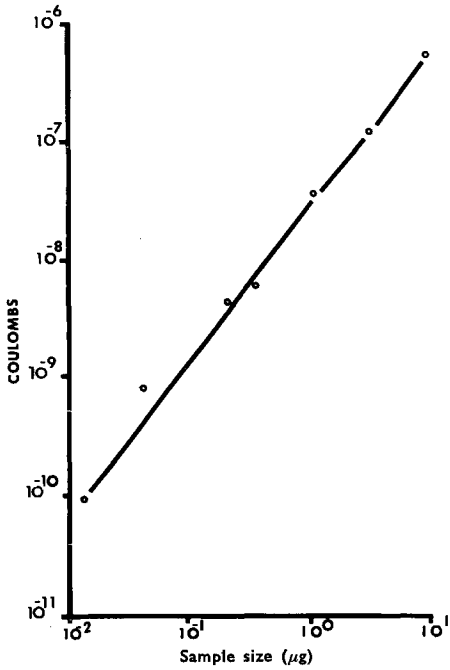
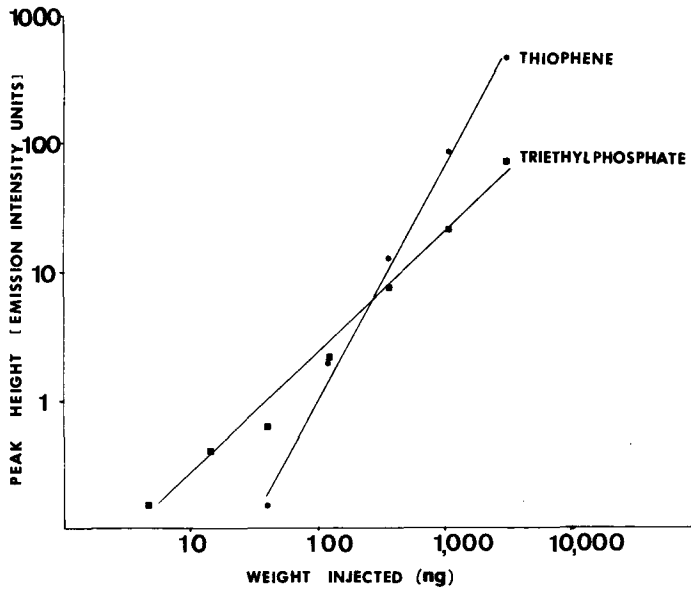Fig. 4. Response of AFID exchange detector (BaCl$_2$) to graded concentrations of trifluorotoluene.

Fig. 5. Response of FPD at 405 nm and at 530 nm to graded concentrations of thiophene and triethyl phosphate.
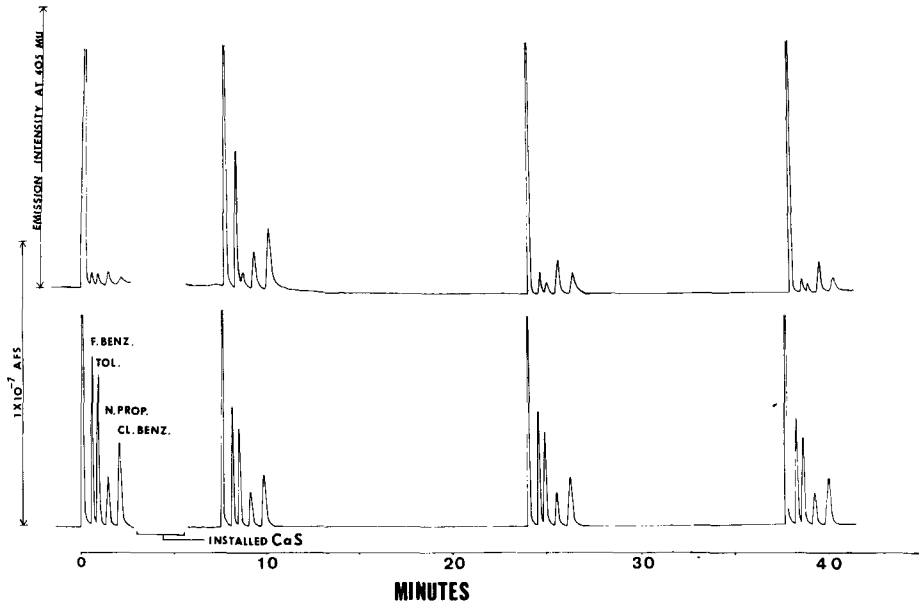
Fig. 6. Response records of CaS-sensitized FPD to repeated injections of 100 nmole each of fluoro-benzene, toluene, nitropropane and chlorobenzene in 1 μl of *n*-hexane, demonstrating change of response with time.

while the phosphorus response increased directly with concentration (Fig. 5). The best sensitivity obtained, in terms of signal-to-noise ratio, was appreciably less than that reported, possibly because of the sub-optimal flame jet geometry and gas mixtures.

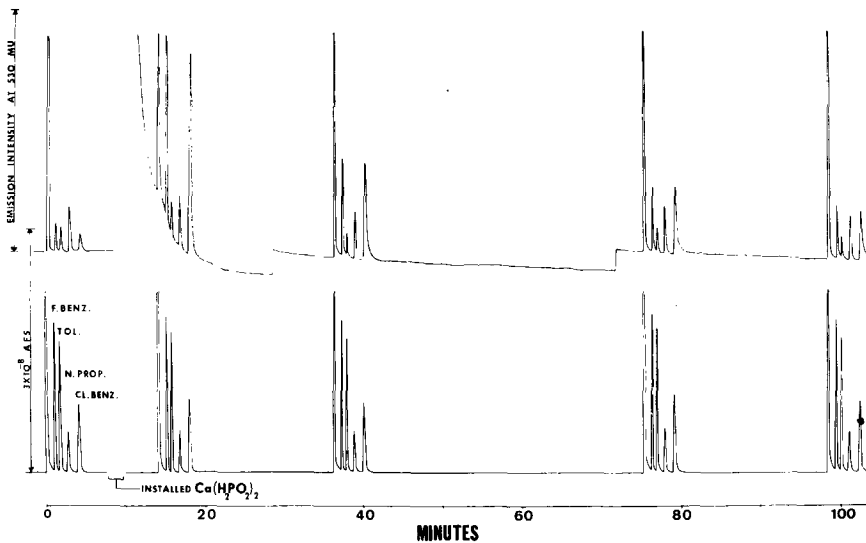When calcium sulphide was used as exchange medium, the response to fluorine

Fig. 7. Response of $Ca(H_2PO_2)_2 + H_2O$-sensitized FPD to repeated injections of 100 nmole each of fluorobenzene, toluene, nitropropane and chlorobenzene, injected at intervals.

was enhanced. The response of the FPD to microgram amounts of each of the test compounds was appreciable even without crystals on the screen. The responses to all compounds, except toluene, were enhanced with calcium sulphide on the screen. The selective enhancement of the response to fluorine was indicated by the larger peak for fluorobenzene in the second record (Fig. 6). The rapidly fading nature of the response was apparent.

Substituting nickel, cobalt(II) and lithium sulphates gave no appreciable increase in baseline current, even when first applied to the screen, and no enhancement of response to any of the test compounds over the response when no exchange media were present.

Substitution of anhydrous calcium hypophosphite crystals and the 530-nm filter resulted in a minimal enhancement of the response to fluorobenzene, which decreased with time more slowly than when calcium sulphide was used. When water was added to the crystals, the responses to fluorine and chlorine were appreciably enhanced, but the response was again short-lived (Figs. 7 and 8). The baseline current also was appreciably increased following the addition of water, and decreased in parallel with the enhanced response.
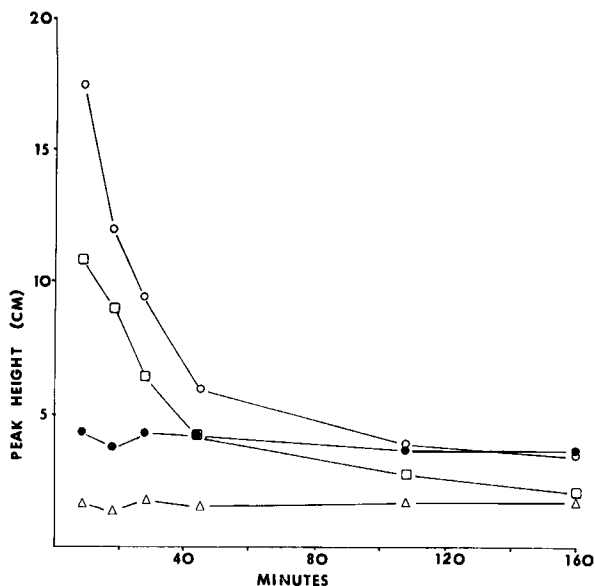

Fig. 8. Response of the $Ca(H_2PO_2)_2$ + H_2O-sensitized FPD to repeated injections of fluorobenzene ($\bigcirc$), toluene ($\triangle$), nitropropane ($\bullet$) and chlorobenzene ($\square$) as a function of time after the installation of fresh $Ca(H_2PO_2)_2$.

DISCUSSION

The experiments described here were designed to test the hypotheses that effective ion exchange could be accomplished if (1) the ion-exchange media were sufficiently heat stable to persist above the hydrogen flame or in the path of the flame gases, (2) the salts formed were less soluble than the salt used as exchange medium, or (3) the acidic gases formed were more volatile.

The marked insolubility of calcium fluoride and the deliquescence of calcium chloride led to the trial of calcium chloride as exchange medium for the detection of fluoride after sodium and potassium chlorides were found to give inconsistent results. Its successful use seemed to be consistent with the hypothesis.

Barium fluoride is less soluble than its chloride, and barium chloride is effective in the same manner as calcium chloride.

The lack of response to nitrogen-containing compounds and toluene was also consistent with the hypothesis.

Thiophene, which presumably gives rise to hydrogen sulphide and more oxidized forms of sulphur, was detected, but with much less sensitivity. In the reverse direction, chlorine-containing compounds released sulphide from the calcium sulphide used in the F.P.D. experiments, suggesting that the equilibrium point of the reaction was intermediate.

Insolubility of the product was not sufficient in itself. Iron(II) chloride did not react appreciably with sulphur and its response to fluorine was consistent with the sparing solubility of iron(II) fluoride in water. Iron(II) chloride showed more non-specific responses to solvent fronts and shorter persistence on the screen, probably as a result of its greater instability to temperature or perhaps to acid.

The short-lived response of calcium sulphide to fluorine and chlorine in the F.P.D. was probably caused by its thermal instability or its lack of deliquescence.

The reaction of calcium hypophosphite to fluorine and chlorine required addition of water.

All these results are consistent with the idea that the exchange medium must be temperature stable and deliquescent, and that the cation forms relatively insoluble or heat stable salts with the heteroatom to be detected. The sensitivity of calcium hypophosphite indicates the possibility of extending the utility of the sensitive F.P.D. for heteroatoms that do not of themselves have characteristic emission spectra. The short-lived response of the salt and its enhancement by addition of water indicates that careful control of temperature and humidity will be required to make a practically useful device.

The specificity of the F.P.D. in these experiments was less than would be desirable, possibly because of the sensitivity of the salt, and perhaps the detector components, to temperature changes.

REFERENCES

1 W. A. Aue and H. H. Hill, *Anal. Chem.*, 45 (1973) 729.
2 R. S. Juvet and R. P. Durbin, *J. Gas Chromatogr.*, (1963) 14.
3 F. M. Zado and R. S. Juvet, *Anal. Chem.*, 38 (1966) 569.
4 R. S. Juvet and R. P. Durbin, *Anal. Chem.*, 38 (1966) 565.
5 S. S. Brody and J. E. Chaney, *J. Gas Chromatogr.*, 4 (1966) 42.
6 A. Karmen and L. Giuffrida, *Nature (London)*, 201 (1964) 1204.
7 A. V. Nowak and H. V. Malmstadt, *Anal. Chem.*, 40 (1968) 1108.
8 C. H. Hartman, *J. Chromatogr. Sci.*, 7 (1969) 163.
9 W. A. Aue, C. W. Gehrke, C. R. Tindle, D. L. Stalling and C. D. Ruyk, *J. Gas Chromatogr.*, 5 (1967) 381.
10 N. F. Ives and L. Giuffrida, *J. Ass. Offic. Anal. Chem.*, 50 (1967) 1.
11 M. Dressler and J. Janák, *J. Chromatogr. Sci.*, 7 (1969) 451.
12 A. Karmen and E. L. Kelly, *Anal. Chem.*, 43 (1971) 1992.
13 A. Karmen and H. Haut, *Anal. Chem.*, 45 (1973) 882.