THE SPECTRAL RESPONSE OF THE ALKALI FLAME DETECTOR*

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SUMMARY

A typical, pellet-type alkali flame detector was monitored photometrically. Its predominant (but not exclusive) mode of response is negative, *i.e.* alkali emission decreases when gas chromatographic effluents are burned in the flame. As a detector for organic halides, the optical emission of the alkali flame appears to simulate some characteristics of its more often used electrical conductivity response. For instance, it is possible to distinguish between chlorine, bromine and iodine, and the (negative) response for chlorides is proportional to the amount of chlorine entering the flame. Calibration curves for selected chlorinated hydrocarbons approach linearity on a logarithmic scale within two orders of magnitude, with minimum detectable amounts between 3–5 ng. Carbon compounds give signals approximately fifty times weaker than monochlorinated compounds. All characteristics considered, the pellet-type alkali source seems to differ considerably in its spectral behavior from other types of sources which have been described in the literature, especially those using a resistance-heated wire coated with sodium sulfate.

INTRODUCTION

Since its inception a few years ago, the alkali flame (thermionic) detector has been the subject of some divergent opinions (for reviews see refs. 1–3). The failure to understand and conclusively prove the mechanism responsible for its response has certainly not detracted from its analytical usefulness. On the contrary, the attempts to gain insight into the mechanism have led to many useful improvements in the detector's configuration.

One of the questions with mechanistic relevance is whether the alkali content of the flame changes with the influx of gas chromatographic (GC) zones and, if so, in what direction. Most authors agree that changes in alkali (light) emission do occur, but differ on most other observations and interpretations. It is safe to state, in retrospect, that small differences in detector geometries, gas flow rates and alkali sources, which were initially considered inconsequential, have led to widely divergent views on detector function and performance.

The picture is further complicated by the fact that in order to obtain a satis-

factory alkali flame (conductivity) response, one is confined to certain detector geo-
metries and flow rates. Spectral measurements of the flame, however, can be, and
sometimes were, carried out under quite different experimental conditions. Conse-
quently, interpretations varied.

Even under meaningful conditions, however, there are apparently several
factors which can influence the spectral characteristics of the alkali flame. Both in-
creases and decreases of alkali emission have been reported[4-11].

In some of our early work with alkali salt tips (similar to those used by
COAHRAN[12]), we had encountered decreases in emission exclusively[9]. It was obvious
that the phenomenon could be utilized as a detector in its own right. We found,
however, that response was not confined to heteroatoms commonly detected through
the conductivity of the alkali flame (P, N, halogen, etc.). Rather, carbon/hydrogen
compounds responded likewise[10].

In an excellent paper published in 1968, NOWAK AND MALMSTADT[4] described a
GC detector also based on monitoring the light emission from an alkali-doped flame.
The authors introduced alkali from a resistance-heated platinum spiral coated with
sodium sulfate, and reported that the detector gave a predominantly positive re-
sponse (increase in alkali emission) and excellent sensitivity and selectivity for halides,
as compared to carbon compounds[4,11]. In a recent study, BOWMAN AND BEROZA[5]
modified this type of detector and applied it to the GC analysis of chlorinated hydro-
carbon insecticides.

It was therefore interesting for us to look anew at the spectral properties of the
pellet-type alkali flame. We used the same general detector configuration and condi-
tions as described in a study of the conductivity response of the flame[13] except that
the common interference filter/photomultiplier arrangement was affixed to the detec-
tor housing. Photometric detectors have been reviewed adequately (e.g. refs. 2, 4,
14, 15). In the following paragraphs, the abbreviation AFPD (for alkali flame photo-
metric detector) will refer to our hybrid of an AFD (alkali flame detector) and an FPD
(flame photometric detector).

EXPERIMENTAL

The AFPD, as shown in Figs. 1 and 2, was mounted on an RAC 1500 column
conditioning oven. Salt pellets were formed from NaF, NaCl, NaBr, Na_2SO_4 and KCl
with a screw-type pellet press. The interference filters were Baird types B-11, 5892A
for sodium and 7665A for potassium. RCA 1P-28 and Hamamatsu R-136 photo-
multiplier tubes were used in a Hilger housing with a slit connector which accommo-
dated filters of 1 in. diameter. A Keithley Model 240-A supplied the power to the tubes
and the signal was amplified by a Keithley 417 picoammeter before going to a Texas
Instruments strip chart recorder. Blank chart paper was used to facilitate subse-
quent reproduction.

The AFPD was tested at various flow rates of hydrogen, air, and the carrier gas,
nitrogen. Test compounds included fluoro-, chloro-, bromo- and iodobenzene, tri-n-
butyl phosphate, aniline, di-n-butyl disulfide and several normal hydrocarbons.

A calibration curve was measured only for chlorine, using several common
chlorinated hydrocarbon insecticides as test compounds. To define any influence upon
response of the molecular structure of compounds entering the flame, equal weight
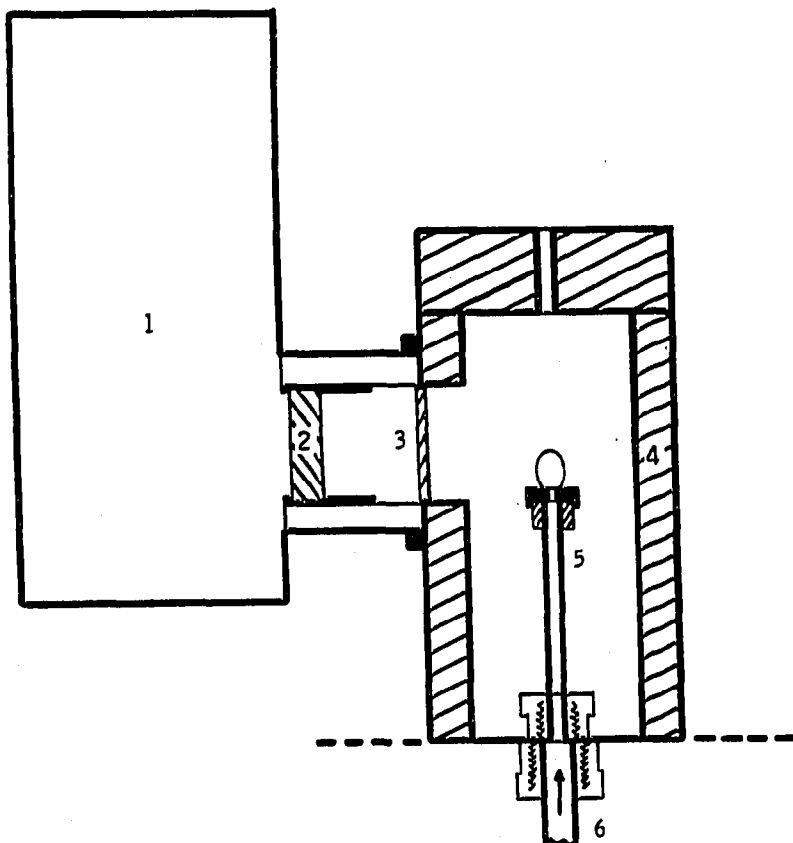
Fig. 1. Alkali flame photometric detector (AFPD). 1 = photomultiplier tube assembly; 2 = interference filter; 3 = quartz window; 4 = Marinite detector housing; 5 = detector jet tip assembly; 6 = GC column.
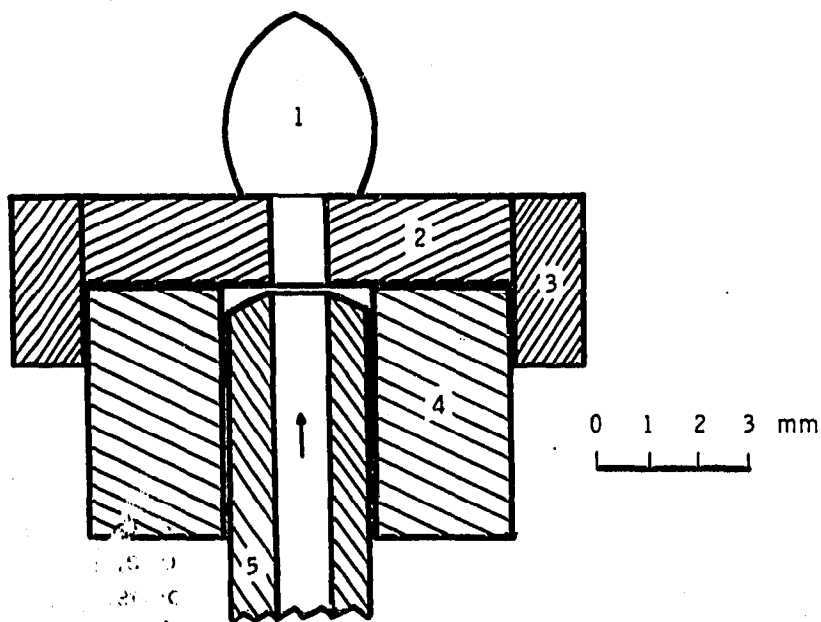

Fig. 2. Alkali flame photometric detector (detail). 1 = hydrogen flame; 2 = salt pellet; 3 = stainless-steel ring; 4 = aluminum collar; 5 = detector jet tip.

amounts of a variety of chlorine-containing compounds were chromatographed. An internal standard was not used, since we assumed that the sensitivity of the AFPD would remain constant throughout that experiment.

RESULTS AND DISCUSSION

Although considerable differences were found among the performances of various salts used in this study, a few general comments can be made which are true of most, if not all, of the pellets.
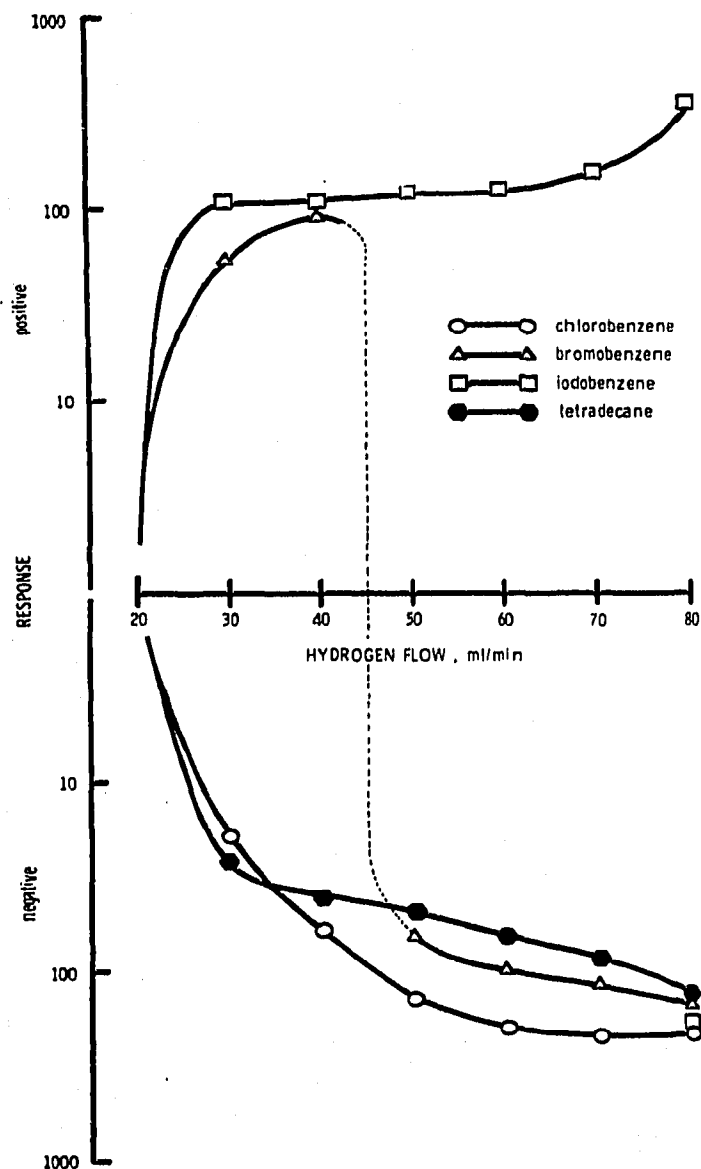

Fig. 3. Halogen response profiles for various hydrogen flows. Injection: 226 ng chlorobenzene, 314 ng bromobenzene, 5 μg iodobenzene and 5 μg tetradecane. Column: 5% Carbowax 20M on 30–100 mesh Chromosorb W-HP, 1.3 m × 4 mm I.D. Pyrex. Oven temperature: 120°. Nitrogen flow rate: 20 ml/min. Air flow rate: 900 ml/min. AFPD, NaCl pellet.

The predominant response of most salts is negative for C/H compounds and halides. Some pellets, however, give rise to positive halide peaks at certain flow conditions; the trend toward positive response decreases markedly in the order $I > Br > Cl$. Chlorobenzene, in fact, always gave a negative signal except when a NaF pellet at very high hydrogen flow rates was used; iodobenzene, in contrast, very often gave positive response.

We found no obvious pattern which could be used to predict on what pellet, or under what flow conditions, positive peaks would be obtained. Fig. 3 shows one of many experiments in which one could differ between Cl, Br and I according to the direction of their responses. (A corresponding chromatogram is shown in Fig. 7.)

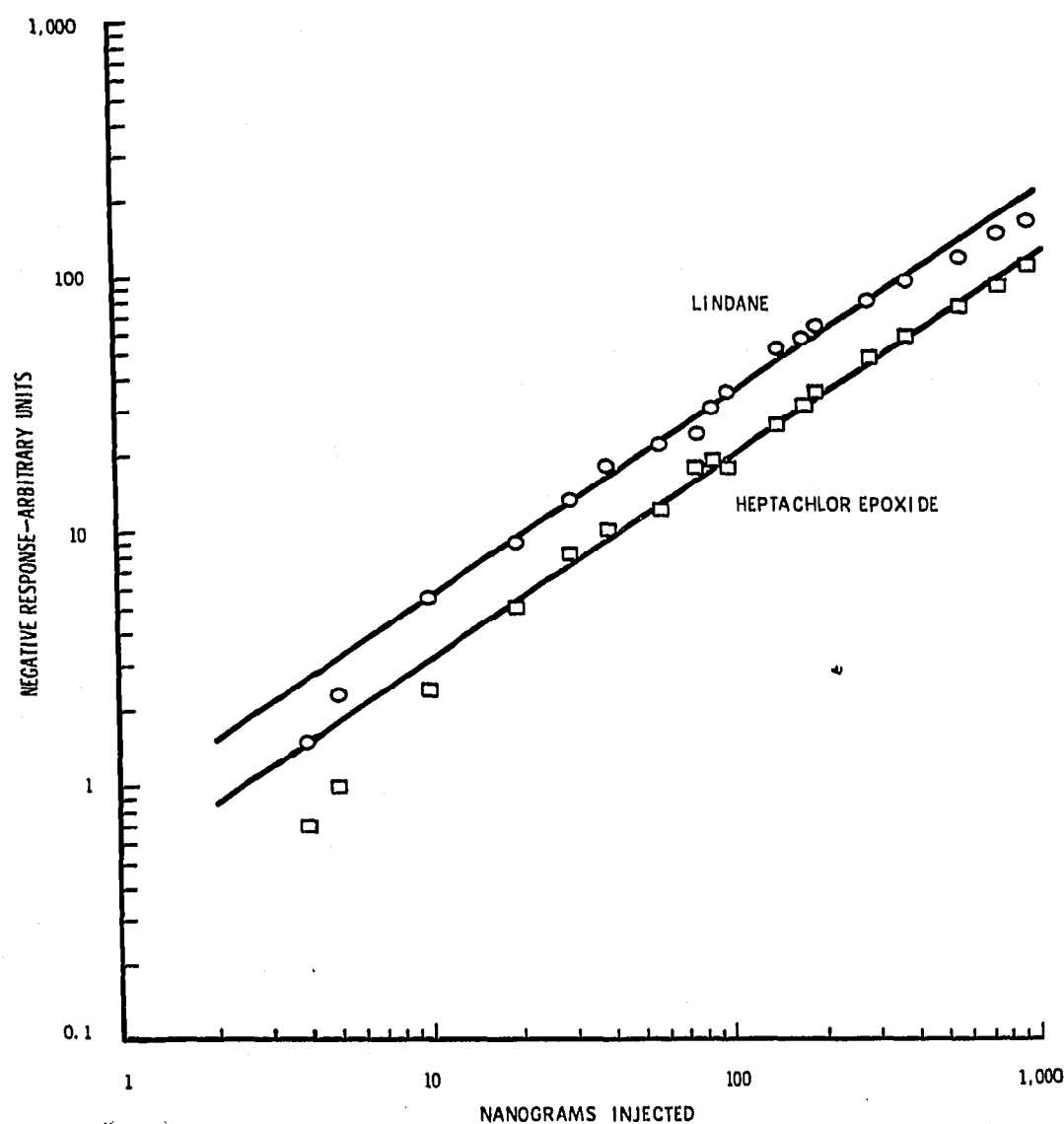Positive response for halides is enhanced by a wire or screen of platinum held in the flame.

Fig. 4. Chlorinated hydrocarbon response. Column: 1.5% OV-17 + 1.95% QF-1 on 100–12 mesh Chromosorb W-HP, 1.8 m × 4 mm I.D. Pyrex. Oven temperature: 210°. Flow rates (ml/min) N₂ 40, H₂ 65, air 900. AFPD, NaCl pellet.

Carbon compounds give a comparatively large response (compare refs. 4 and 5). The signal amplitudes for halides are usually less than a hundred times those for equal weights of C/H compounds, with selectivity decreasing in the order Cl>Br>I. Typical minimum detectable amounts are 3 ng of heptachlor and 100 ng of tetradecane.

Phosphorus gives negative response at low, positive response at high hydrogen flows on a sodium chloride pellet. The best selectivity for tri-*n*-butyl phosphate (as compared to *n*-tetradecane) is in excess of 100, its minimum detectable amount being about 3 ng. However, phosphate peaks can tail severely depending on the nature and age of the pellet. Nitrogen-, sulfur- and fluorine-containing compounds were briefly tested but failed to respond in any noteworthy fashion.

Calibration curves for chlorinated hydrocarbon insecticides are roughly linear within two orders of magnitude on a logarithmic plot (Figs. 4 and 5).

As shown in Fig. 6, the amount of chlorine entering the flame in the form of various mono- and polyhalides is apparently the only factor determining response — there is no indication that the organic structure exerts a significant influence (compare ref. 5).
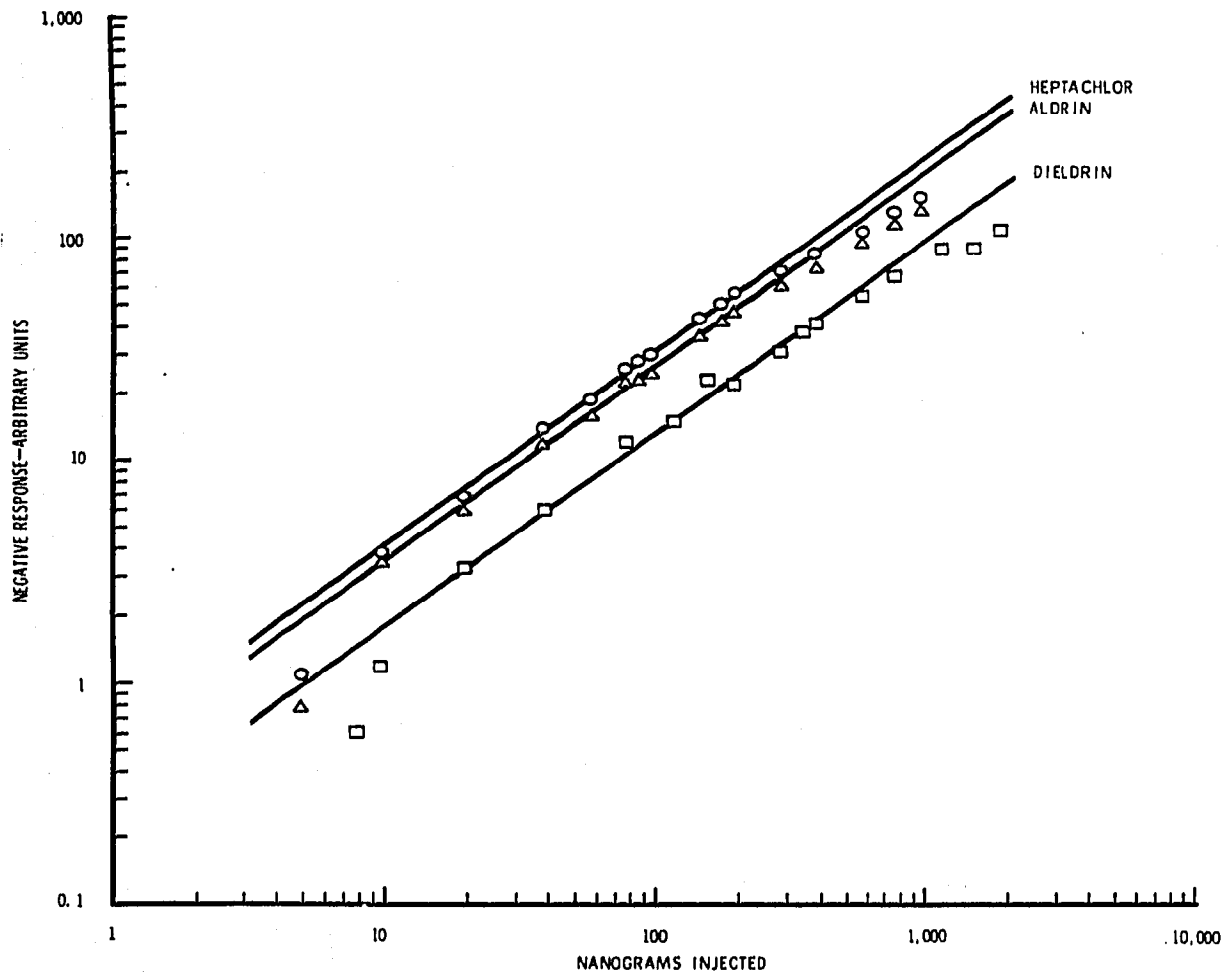

Fig. 5. Chlorinated hydrocarbon response. Column: 1.5% OV-17 + 1.95% QF-1 on 100–120 mesh Chromosorb W-HP, 1.8 m × 4 mm I.D. Pyrex. Oven temperature: 210°. Flow rates (ml/min): 40, H₂ 65, air 900. AFPD, NaCl pellet.
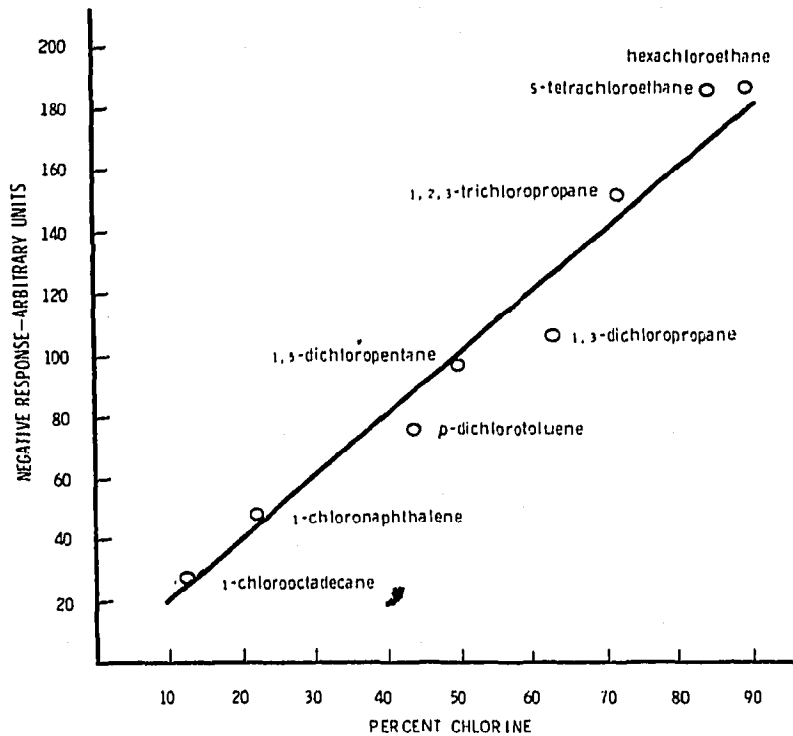
Fig. 6. Response as a function of chlorine content. Injection: 200 ng each. Column: 5% Carbowax 20 M on 80–100 mesh Chromosorb W-HP, 1.3 m × 4 mm I.D. Pyrex. Oven temperature: 120° or 190°. Flow rates (ml/min): N₂ 27, H₂ 80, air 900. AFPD, NaCl pellet.
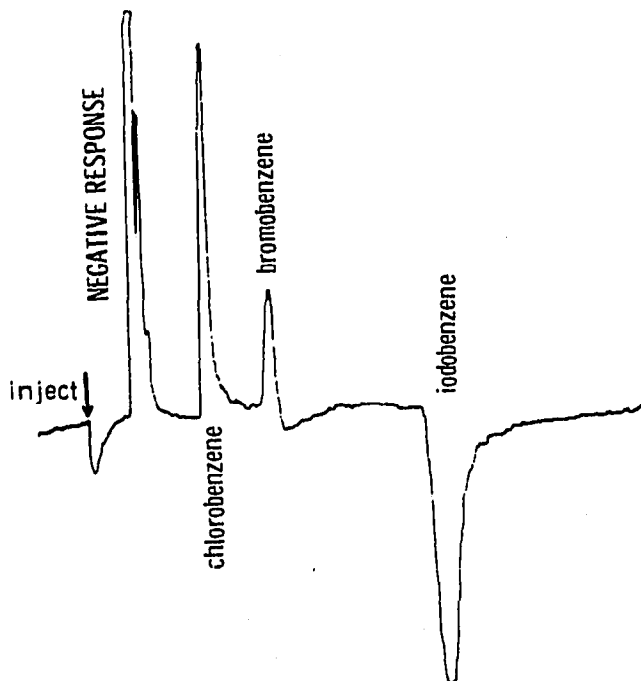

Fig. 7. Chromatogram of halogenated benzenes. Injection: 0.5 μl containing 0.113 μg chlorobenzene, 0.157 μg bromobenzene, 2.5 μg iodobenzene. Column: 5% Carbowax 20 M on 80–1n mesh Chromosorb W-HP, 1.3 m × 4 mm I.D. Pyrex. Oven temperature: 120°. Flow rates (ml/m: .. N₂ 40, H₂ 80, air 900. AFPD, NaCl pellet. 1 × 10⁻⁷ a.f.s.

Pellets age within the first days of use. Response characteristics change quite significantly before a steady state is reached. These changes may involve direction of response, peak tailing (especially with phosphates) and, of course, noise and drift. Once conditioned, however, pellets have a useable life span in excess of one month.

A similarity, at least on a formal basis, exists between chromatograms of halides by the AFD and AFPD. For instance, Fig. 7 looks very similar to tracings from an AFD [13,16]. It is obvious that both AFD and AFPD can be adjusted to distinguish between chlorides, bromides and iodides according to the direction of their responses.
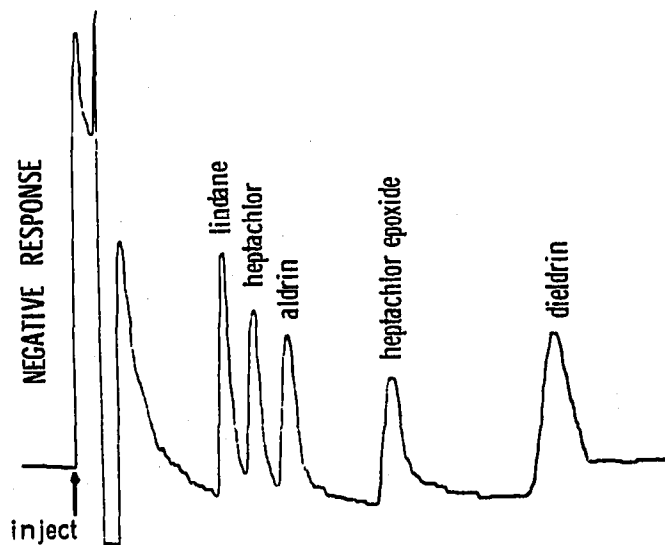

Fig. 8. Chromatogram of pesticides. Injection: 40 ng each of lindane, heptachlor, aldrin and heptachlor epoxide, and 80 ng of dieldrin. Column: 1.5% OV-17 + 1.95% QF-1 on 100–120 mesh Chromosorb W-HP, 1.8 m × 4 mm I.D. Pyrex. Oven temperature: 210°. Flow rates (ml/min): N_2 45, H_2 65, air 900. AFPD, NaCl pellet. 1 × 10^{-8} a.f.s.

Although chlorinated hydrocarbon insecticides can be well detected (Fig. 8), the AFPD can not be recommended for use in residue work, since its selectivity for chlorine is comparatively low and several other excellent detectors exist for these types of analyses. In fact, the "sodium sulfate-sensitized flame"[4,5] would be a better choice than the AFPD for residue analysis. The capability of the AFPD to distinguish between several heteroatoms, however, could perhaps be used to some advantage in specialized applications.

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