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## THE DETERMINATION OF CHLORINATED HYDROCARBONS USING THE NEGATIVE ALKALI FLAME DETECTOR RESPONSE\*

STANISLAV LAKOTA\*\* AND WALTER A. AUE\*\*\*

*Experiment Station Chemical Laboratories, University of Missouri, Columbia, Mo. 65201 (U.S.A.)*

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## SUMMARY

Under specific instrumental conditions, the alkali flame detector will give negative peaks for chlorine-containing compounds, and positive peaks for Br-, I-, N-, or P-containing compounds. In such a mode, the detector can be used for qualitative and quantitative determination of chlorides. It discriminates against carbon compounds by approximately three orders of magnitude, detecting a minimum amount of 1 ng of chlorobenzene. The negative response can be used to detect chlorinated hydrocarbon pesticide residues in soil at levels between 0.01 and 10 p.p.m. without purification of an exhaustive hexane extract.

## INTRODUCTION

Gas-liquid chromatography combined with electron capture detection is by far the most successful method in the determination of chlorinated hydrocarbon residues. The method possesses superior sensitivity, and, if proper purification procedures are followed, yields quantitative results. In the determination of very low amounts of residues, however, special problems arise. When extraneous peaks originating from co-extractants start to appear in greater number in the chromatogram, there is usually some doubt shed on the identity of the peaks supposedly representing chlorinated hydrocarbons. Although the use of a different type of GLC column will generally dispell some of the doubt, the accuracy of the analysis is by no means assured. To complicate matters further, none of the commonly employed means of establishing identity (IR, MS, etc.) are easy to use with very low pesticide levels.

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\*\* Present address: ul. Doswiadczalna 11, Instytut Przemystu Organicznego, Pszczyna, Poland.

\*\*\* To whom reprint requests should be directed.

To a much lesser degree than the electron capture detector (ECD), the alkali flame detector (AFD, 'thermionic detector', 'Karmen-Giuffrida detector', 'phosphorus detector', refs. 1 and 2) has been used for the detection of volatile halides (refs. 3-9 and others). Most authors agree that its response to halogen is inferior to phosphorus; and that the ECD is by far preferable to the AFD for the analysis of chlorinated hydrocarbons (*e.g.* ref. 17).

It is a well-known fact to most analysts working with the AFD that it may produce negative peaks at certain flow conditions. The reason for this behavior is unknown.

This study was designed primarily to investigate this effect and to find instrumental conditions, at which a satisfactory negative response for chlorides in general and chlorinated hydrocarbon insecticides in particular, could be obtained; maintaining at the same time the positive response of the detector toward other heteroatoms (Br, I, N, P) and carbon compounds in general. Such detector characteristics would make it feasible to distinguish the volatile chlorides from any other compounds appearing on the chromatogram. As a secondary objective, the application to crude (non-purified) soil extracts and a subsequent attempt at quantitation were considered important.

#### *Preliminary experiments*

Former studies of the AFD<sup>9</sup> had shown that different elements exhibit response maxima in different areas of the flame. Small changes in the instrumental parameters (*i.e.* the H<sub>2</sub>, N<sub>2</sub>, and air flow, the shape and size of the electrode, and the shape of the alkali source) can have a marked influence on the response of various species. In order to arrive at the best conditions for an optimal (negative) response/noise ratio, the electrode and alkali source dimensions were evaluated in preliminary experiments. Single loop platinum electrodes of inner diameters 3, 5 and 7 mm were used, matched with alkali sources similar to one described earlier<sup>10</sup>. Ceramic beads coated with rubidium sulfate, pressed and drilled rubidium and potassium chloride pellets (ref. 11, compare with ref. 12), and pressed and drilled rubidium sulfate pellets were tested. The latter, although the most difficult to prepare, gave the best results and were used exclusively for later studies. High-speed drilling was used to obtain bores between 1 and 4 mm in 1 mm steps. This produces a variety of flame shapes from a tall and narrow flame to a short and broad one. Twelve combinations of electrode and alkali source were evaluated with chlorobenzene, bromobenzene, iodobenzene, benzylamine, and tri-*n*-butylphosphate, and the direction and maximum of response measured over electrode distances ranging from 1 to 10 mm above the alkali source at a variety of flow conditions.

Negative response could be obtained for each of the active elements at particular conditions. The exact location and the maximum of the negative range, however, depended to a great deal on the particular alkali source (bead or pellet), and were not *exactly* reproducible with another source of approximately the same dimensions. This was obviously caused by the fact that, in our experiments, the surface structure and dimensions of a pellet were not completely reproducible, and the shape and the alkali content of the flame varied accordingly.

We decided from these preliminary studies to use a 1 mm bore pellet and a 7 mm I.D. electrode for the detection of chlorides.

## EXPERIMENTAL

A Barber-Colman 5320 gas chromatograph was modified as follows: The aquarium pump air supply was replaced with a high pressure air cylinder with regulator and needle valve; the hydrogen supply was taken from a tank through a differential flow controller and a flow equalizer-activated carbon filter arrangement. The Variac-controlled heating system of the column bath was replaced by a lab-made thermostat, and the injection port modified by drilling through the injection block and extending the glass column up to the septum, to allow direct on-column injections into a 'swept-septum' configuration.

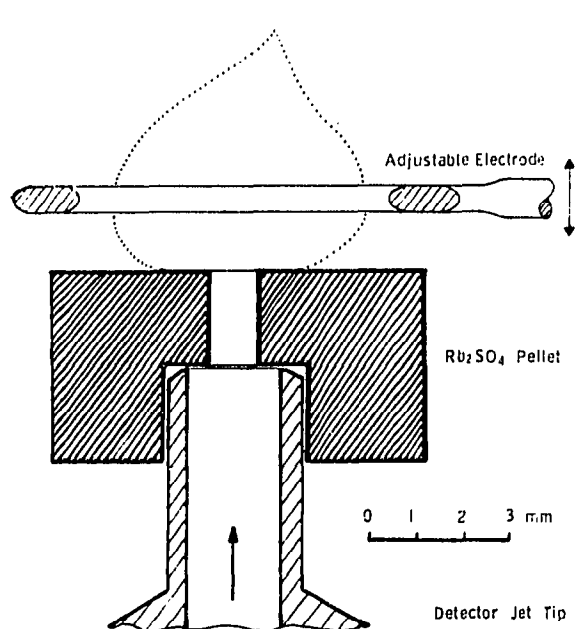


Fig. 1. Alkali-flame detector modification.

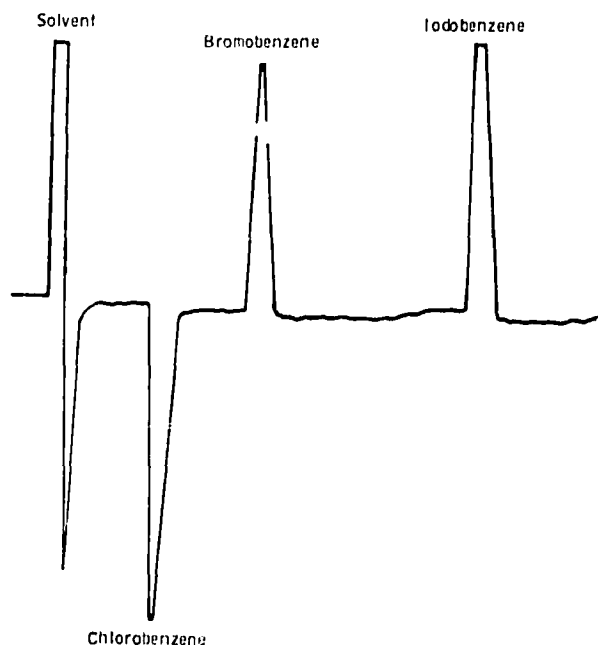


Fig. 2. Detector selectivity. Electrode: 7 mm I.D., set 4 mm above the pellet, + 240 V. Pellet: pressed  $\text{Rb}_2\text{SO}_4$ , 1 mm bore. Flow rate:  $\text{H}_2$  33,  $\text{N}_2$  50, air 215 ml/min.

A coiled pyrex column of 1.7 m length and 3.5 mm I.D. was filled with a mixed stationary phase suitable for pesticide analysis, 9.8% DC-200 + 15.8% QF-1 (50/50 w/w, see ref. 13) on Anakrom ABS, 90/100 mesh, prepared in fluidized bed. The basic design of the AFD with a vertically adjustable electrode as described earlier<sup>14</sup>, was used with the following modifications: A steel cylinder surrounded the flame area; it was cut to allow free movement of the electrode. This electrode was a slightly flattened single loop of 7 mm I.D., made from platinum wire 1 mm thick. The alkali source was a pressed, high-purity rubidium sulfate pellet (K & K, 99.9%  $\text{Rb}_2\text{SO}_4$ , fractionally recrystallized from double distilled water). With a screw-type press similar to models used in IR work, pellets were produced from finely ground, slightly moist rubidium sulfate. The pressing and high-speed drilling of the pellets takes some practice before a satisfactory product can be obtained. A good pellet, however, will perform for several months without apparent deterioration. A scheme of the detector is shown in Fig. 1.

### Optimization of detector response

The height of the electrode and the flow rates (especially  $H_2$ ) were changed in small increments while repeatedly injecting a mixture of chlorobenzene, bromobenzene, and iodobenzene in hexane, until an optimal response/noise ratio for negative chlorine response had been obtained (e.g. Fig. 2). In a typical case, the pellet bore was 1.0 mm and the electrode approx. 1.5 mm (1.4–1.6 mm) above the  $Rb_2SO_4$  surface. The hydrogen flow was 33, nitrogen 50, and air 215 ml/min. These conditions were then used to determine response factors for all other tested elements (Fig. 3).

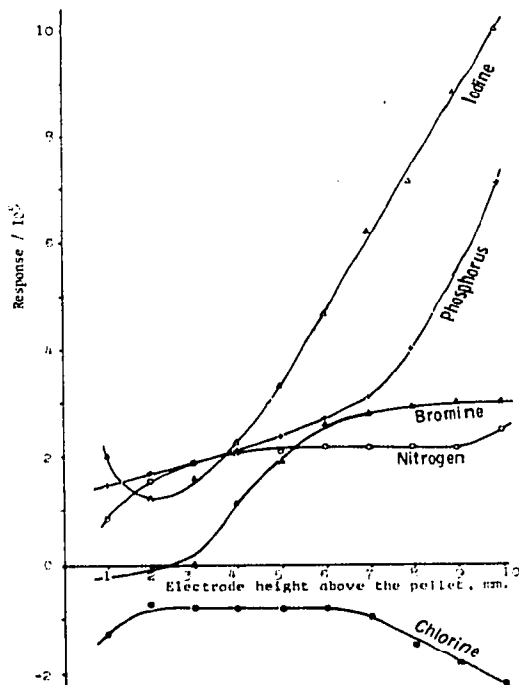


Fig. 3. Effect of electrode height. Electrode: 7 mm I.D. Pellet: pressed  $Rb_2SO_4$ , 1 mm bore. Potential: + 240 V. Flow rate:  $H_2$  33,  $N_2$  50, air 215 ml/min. Injections: 1  $\mu$ l of hexane solutions containing 1  $\mu$ l/ml each of chlorobenzene, bromobenzene, iodobenzene and benzylamine and 10  $\mu$ g/ml of tri-*n*-butylphosphate.

The response was calculated as

$$R = \text{Peak area (cm}^2) \cdot \frac{\text{attenuation}}{\text{sensitivity}} \cdot \frac{1}{\text{weight injected (g)}}$$

in  $\text{cm}^2/\text{g}$  for all elements except phosphorus. To keep phosphorus within the limits of Fig. 3, its response was calculated in  $\text{cm}/0.1 \text{ g}$ . For purposes of comparison, 1  $\text{cm}^2$  is roughly equivalent to  $7 \times 10^{-6}$  Coulombs.

### Determination of selectivity ratio

Essentially the same approach as reported earlier<sup>14</sup> was used to illustrate the practical performance which can be expected from such a system. At conditions optimized for negative chlorine response, Lindane was compared to *n*-octadecane on a

weight basis. Taking the FID response as a standard, the selectivity ratio (SR) was calculated as in the following example:

$$SR \left( \frac{\text{Lindane}}{\text{octadecane}} \right) = \left( \frac{A_{Cl}}{A_C} \right)_{\text{alkali flame}} \times \left( \frac{A_C}{A_{Cl}} \right)_{\text{FID}}$$

wherein  $A_{Cl}$  and  $A_C$  represent the peak areas obtained from the chlorocompound and the hydrocarbon, respectively.

### Soil spiking and analysis

Menfro silt loam with no history of pesticide treatment (courtesy of Dr. BILLY TWEEDY, Department of Plant Pathology, University of Missouri, Columbia) was spiked with 10, 1, 0.1 and 0.01 p.p.m. of Lindane, Aldrin and heptachlorepoide, as well as Dieldrin at double and *p,p'*-DDT at five times this concentration (heptachlor was inadvertently omitted). Samples of the spiked soil (approx. 25 g) were placed into thimbles and extracted for 16 h in a Soxhlet or 8 h in a Goldfish apparatus (Fisher Scientific Company, St. Louis, Mo.) with hexane. The resulting extracts were taken to a volume of 1 ml in a Kuderna-Danish evaporator, and 1  $\mu$ l injected. In case of the 0.01 p.p.m. spiked soil, the extract was concentrated to 0.1 ml. Solutions of pesticide standards (Fig. 4, Parathion was added to show the positive response for phosphorus) were used to determine linearity of the detector (Fig. 5) and the recovery in the soil extracts. After chromatographic separation at 190° (Fig. 6), the area of the peaks was determined for use in a calibration curve (Fig. 7).

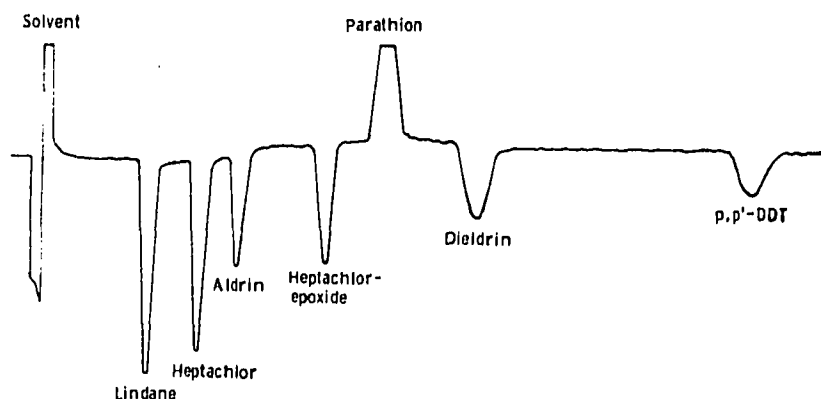


Fig. 4. Standard mixture of pesticides. Electrode: 7 mm I.D., set 1.5 mm above the pellet. Pellet: pressed  $Rb_2SO_4$ , 1 mm bore. Potential: + 240 V. Flow rate:  $H_2$  33,  $N_2$  50, air 215 ml/min. Column: 9.8% DC-200 + 15.8% QF-1 (50/50 w/w) on Anakrom ABS, 90/100 mesh, prepared in fluidized bed. Column bath 190°, injection port 220°, detector 210°. Injection: 1  $\mu$ l of a hexane solution containing 10 p.p.m. of each of the chlorinated hydrocarbons and 1 p.p.m. of Parathion.

## RESULTS AND DISCUSSION

Considering the simplicity of the alkali flame detector design, it is amazing how many different modes of performance it is capable of assuming. In this study, some basic parameters were altered in preliminary experiments in order to find a system, which would produce negative response to chlorine containing compounds with a response/noise ratio acceptable for pesticide residue analysis. Several configurations showed promise; Fig. 1 shows the principal configuration of the detector version finally chosen for detailed evaluation.

After this system had been optimized for chlorine response, the minimum detectable amount of chlorobenzene was approx. 1 ng. The minimum detectable amounts of several chlorinated hydrocarbons were somewhat lower, but still approximately three orders of magnitude higher than those obtainable with an ECD. The response of the ECD, however, depends to a much higher degree on the amount of halogen substitution than the AFD, whose response is proportional to the amount of halogen introduced.

While the AFD is clearly inferior to the ECD in terms of sensitivity, it can provide a qualitative test for the presence of chlorine in a compound available only in trace quantities. Obviously, this test will be erroneous if the compound contains phosphorus in addition. The results obtainable from compounds which contain other

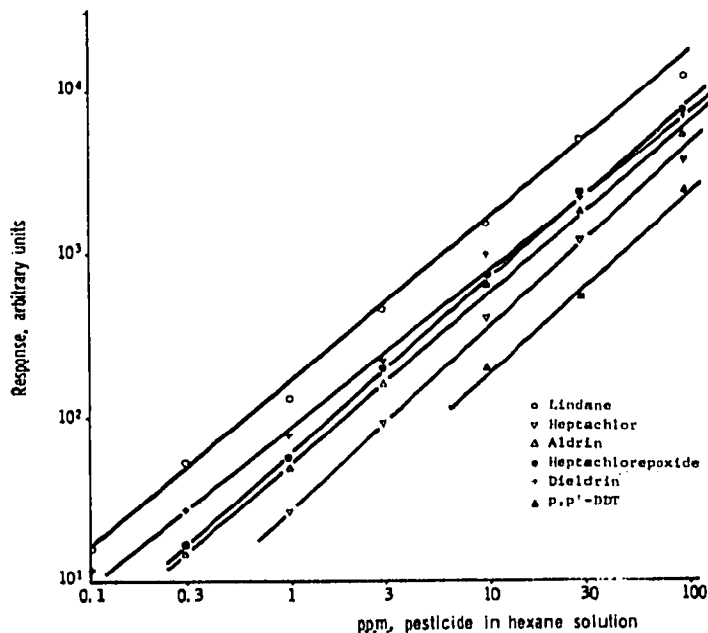


Fig. 5. Linear range of detector response. Electrode: 7 mm I.D., set 1.5 mm above pellet. Potential: + 240 V. Pellet: pressed  $\text{Rb}_2\text{SO}_4$ , 1 mm bore. Flow rate:  $\text{H}_2$  33,  $\text{N}_2$  50, air 215 ml/min. 1  $\mu\text{l}$  injections.

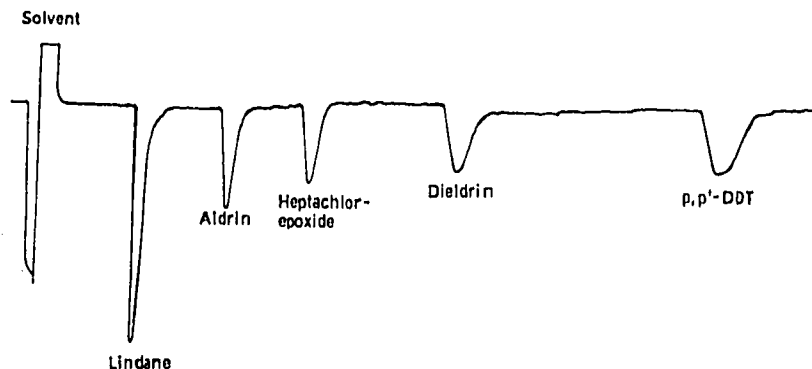


Fig. 6. Crude soil extract. Menfro Silt Loam spiked with 1 p.p.m. each of Lindane, Aldrin, heptachlorepoixide, 2 p.p.m. of Dieldrin and 5 p.p.m. of *p,p'*-DDT. Soxhlet extraction with hexane. Electrode: 7 mm I.D., set 1.5 mm above the pellet. Pellet: pressed  $\text{Rb}_2\text{SO}_4$ , 1 mm bore. Potential: + 240 V. Flow rate:  $\text{H}_2$  33,  $\text{N}_2$  50, air 215 ml/min. Column bath 185°, injection block 220°, detector 200°.

halogens or nitrogen, besides chlorine, would suffer from some degree of ambiguity, depending on the particular conditions involved. In actual residue analysis, however, these cases are relatively rare and the analyst is more often faced with the question, whether a particular peak in the chromatogram represents a chlorinated hydrocarbon residue or an unknown (and unwanted) co-extractant. For these cases, the AFD, functioning in a negative mode for chlorine, should allow an easy decision. A similar answer can be obtained from the microcoulometric detector, which does not, however, distinguish between the halogens.

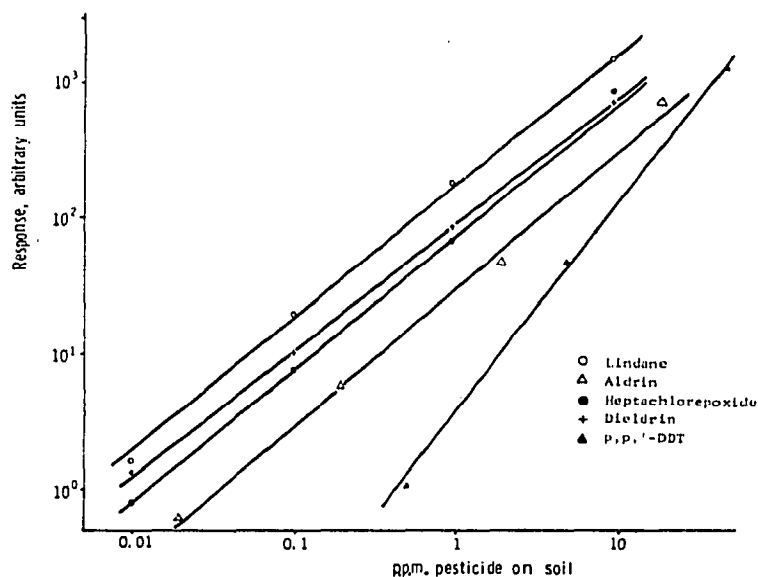


Fig. 7. Chlorinated hydrocarbons from soil. Menfro Silt Loam spiked with a mixture of Lindane, Aldrin, heptachlorepoixide, Dieldrin and *p,p'*-DDT (weight ratio 1:1:1:2:5); Soxhlet extracted with hexane. Electrode: 7 mm I.D., set 1.5 mm above the pellet. Pellet: pressed  $\text{Rb}_2\text{SO}_4$ , 1 mm bore. Potential: + 240 V. Flow rate:  $\text{H}_2$  33,  $\text{N}_2$  50, air 215 ml/min. Column: 9.8% DC-200 + 15.8% QF-1 (50/50 w/w) on Anakrom ABS, 90/100 mesh, prepared in fluidized bed. Column bath 185°, injection port 220°, detector 200°.

Fig. 2 shows an example of the detector set to distinguish clearly between chlorine and the other halogens. (Fluorine is not comparably enhanced in the AFD.) Once the detector dimensions and flow conditions are given, the distance of the electrode from the  $\text{Rb}_2\text{SO}_4$  surface, 'electrode height', is the determining parameter for size and sign of the response and the consequent discrimination against other elements (Fig. 3). It should be emphasized that such response profiles can vary a great deal with small changes in detector dimensions and flow conditions. For the chosen set of conditions, however, chlorine response was always negative, bromine either negative or positive and the other elements were positive throughout the range of electrode heights. The question what setting to use in a particular analysis depends on a number of factors, such as the response/noise ratio and the selectivity ratio towards unwanted co-extractants. For example, the analysis for hydrocarbons in soil (Figs. 6 and 7) called for a high selectivity ratio towards carbonaceous material and low-noise characteristics, which were best achieved with an electrode height around 1.5 mm.

The detector linearity was tested with a variety of chlorinated hydrocarbon standards (Fig. 4; Parathion is included to show the positive response for phosphorus).

The results of this study are satisfactory (Fig. 5), with aberrations apparently due to changes in detector sensitivity during the course of the experiment. For accurate measurements, an internal standard may have proved advantageous.

The 'solvent peak' on the chromatograms (Figs. 2, 4, and 6) shows a negative and a positive part. This is due to a disturbance of the detector, since smaller amounts of carbon compounds give symmetric, positive peaks. If the solvent peak is kept on scale, its area is almost entirely positive.

The discrimination of the AFD against carbon compound background lies in a range, which could permit gas chromatographic analysis of unpurified extracts from various types of samples, provided their residue content were not extremely low. As a measure of this discrimination, the selectivity ratio (SR) based on a comparison with the response characteristics of the ubiquitous hydrogen flame detector, was measured with Lindane and octadecane as model substances for a chlorine and a carbon compound.

The value obtained was  $SR(\text{Lindane/octadecane}) = 3100$ , which stems from the ratio of responses from the AFD obtained for equal weight amounts (1040) and the same ratio from a regular FID (0.33). This particular approach to characterize selectivity was chosen from an entirely practical viewpoint. The SR values depend, of course, on the response of the standard in the FID and will, therefore, vary with the choice of the standard. They provide, however, a good practical indication of the amount of interference which can be expected to arise from volatile co-extractants; or the selectivity to be gained for chlorocompounds *vs.* hydrocarbons when the analysis is switched from a FID to an AFD.

Although phosphorus response is still greater than chlorine response — as seen from  $SR(\text{Lindane/tri-}n\text{-butylphosphate}) = 0.105$  at conditions optimized for chlorine — the figure is much better than values found in the literature, which generally range two or three orders of magnitude lower. Using different pellet and electrode dimensions, this value could quite conceivably be shifted further in favor of chlorine.

To test the detector with an actual analysis, the common case of a soil analysis for chlorinated hydrocarbons was chosen. No purification of the extract was attempted; however, the initial extraction was done in a Soxhlet or Goldfish apparatus with hexane for an extended period of time; a procedure designed to minimize the amount of co-extractants<sup>15,16</sup>. Since continuous extractions run practically unattended, the amount of time spent for sample preparation was minimal.

As can be seen from Figs. 6 and 7, the results obtained would satisfy the requirements for a screening analysis. The recoveries for all pesticides except *p,p'*-DDT are acceptable at the 10–0.1 p.p.m. levels (80–100%). The scope of this work did not include the analysis of vegetables, fruits, tissues, or biological fluids, and none of these types of analyses were attempted. Judged from the results of a study involving nitrogen containing herbicides with similar selectivity ratios<sup>14</sup>, such an investigation would be definitely worthwhile.

It should be noted in the context of routine analysis, that we found the AFD quite temperamental in the described mode. It is easily disturbed, prone to sudden baseline shifts, and constant attention of the operator is required in the high-sensitivity ranges. Although the device is simple (and inexpensive), it takes time to adjust the conditions for optimal performance. Thus, it will definitely not replace the EC detector for quantitative analyses.



In summary, the AFD in its described version, may have applications for the qualitative and semi-quantitative analysis of volatile halides in screening and identity tests.

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