The sensitivity of the method is established at 0.1 p.p.m. Although it is possible to inject larger amounts of sample material to double or even triple the sensitivity, this tends to foul the system with extraneous crop extractives. In the case of cottonseed, larger samples cause peak broadening. Using the above procedure 0.1 p.p.m. produces an area on the recorder strip chart of about 0.5 square inch. This area can be measured with a polar planimeter with good accuracy.

In only one case was there any interference from peaks for crop extractives and in that case the value was less than half of that corresponding to 0.1 p.p.m. of Chemagro 2635. In no case did a control peak equal the response for 0.1 p.p.m. of fungicide.

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PESTICIDE ANALYSIS

Simultaneous and Selective Detection of Phosphorus, Sulfur, and Halogen in Pesticides by Microcoulometric Gas Chromatography

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Pesticides containing phosphorus, sulfur, or chlorine are separated from one another by gas chromatography and reduced to PH_3, H_2S, or HCl, respectively, with molecular hydrogen at 950° C. All three gases can be measured simultaneously with a microcoulometric titration cell equipped with silver electrodes. Alternatively, PH_3 and H_2S can be measured selectively by inserting a subtraction unit or GSC column between the outlet of the reduction tube and the inlet of the titration cell.

MICROCOULOMETRIC gas chromatography is widely used for the analysis of pesticides and drugs containing chlorine and sulfur. The compounds are separated from one another on a chromatographic column and then burned to yield CO_2, H_2O, HCl, and SO_2. HCl is measured specifically with a titration cell equipped with silver electrodes, while SO_2 is measured with an I_2/I^- cell. Details of this method are described by Coulson *et al.* (*3*).

This procedure has many advantages compared to other methods of analysis. It is highly sensitive, many compounds can be separated in a single operation, background from hydrocarbon and oxygenated hydrocarbon impurities in the sample is virtually eliminated, and interference from column bleed and tailing of the solvent peak is minimized. However, this method is not applicable to the detection of organic phosphates. The phosphate moiety is probably converted to P_4O_{10} in the combustion tube, but fails to emerge from it—probably because of its low vapor pressure and high reactivity. Consequently, a method was developed in which the column effluent is reduced with molecular hydrogen at 950° C. Phosphates are converted to PH_3, organically bound sulfur to H_2S, and organically bound chlorine to HCl. All three of these gases precipitate silver ion, and thus can be measured with a microcoulometric titration cell equipped with silver electrodes. This method is particularly suitable for the analysis of phosphorus-containing compounds, since phosphine is a chemically stable gas boiling at −87.8° C. By contrast, P_4O_{10}, which is formed on oxidation, sublimes at 360° C.

If the effluent from the reduction tube is passed directly into the titration cell, PH_3, H_2S, and HCl are measured simultaneously with a relative sensitivity of 2:2:1 if these gases are present. However, if a short subtraction tube containing Al_2O_3 is inserted between the exit line of the reduction tube and the inlet of the titration cell, H_2S and HCl are subtracted quantitatively. PH_3 passes through this packing unchanged, and thus can be measured with absolute specificity. PH_3 and H_2S can be measured in the presence of one another by inserting a short GSC column containing silica gel between the reduction tube and titration cell. Thus ronnel, which contains phosphorus, sulfur, and chlorine atoms, yields two peaks, the first of which represents PH_3 and the second H_2S. HCl is bound irreversibly by this column. Thus the method can be used to detect phosphorus alone, measure phosphorus and sulfur independently when they occur in the same compound, or measure the sum of phosphorus, sulfur, and chlorine. Moreover, sulfur bonded directly to phosphorus can be measured directly without interference from PH_3 by operating the reduction tube at a lower temperature (700° C.).

Reagents

Electrolyte. The electrolyte used in the Ag/Ag^+ titration cell was a 70 to 75% solution of acetic acid in water containing 0.2% Triton X-35, obtained from Rohm & Haas.

Aluminum oxide, Alcoa alumina, activated, grade F-20, 80- to 200-mesh,

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W. H. Curtin Co., Catalog No. 31798B.

Silica gel, 30- to 60-mesh, chromatographic grade, Micro-Tek Instruments, Catalog No. GCA-558.

Apparatus

A Micro-Tek Model 2500 gas chromatograph with a temperature programmer and the oven modified to accept a special column design (Figure 1) was used as the basic instrument. A Dohrmann Instrument Co. Model T-200 titration cell and a Model C-100 microcoulometer were used to detect the reactive gases generated in the reduction furnace.

The column was a 1-meter × 8-mm. o.d. × 3-mm. i.d. glass U-tube connected to about 12 cm. of 6-mm. o.d. tubing that served as the column inlet. The column inlet passed through a $^1/_4$-inch Swagelok bulkhead connector fastened to the oven top, which supported the column. A flash heater was positioned above the connector. The heater was a 1-cu. inch block of aluminum drilled to fit over the tube. The heater block contained a 50-watt cartridge heater supplied by Wilkens Instrument Co. Injection was made through a $^1/_4$-inch Swagelok T that slipped over the 6-mm. o.d. glass tubing. The entrance of the T was sealed from the atmosphere with a silicone rubber septum. A silicone rubber O-ring was used to form the seal on the tube at the bottom of the Swagelok T. Hydrogen was used as the carrier gas for chromatography, and was introduced into the system through the side opening of the Swagelok T.

The downstream end of the chromatographic column was connected with a graded seal to a 35-cm. length of quartz tubing, 7-mm. o.d. by 5-mm. i.d. This quartz tube extended through the oven top, and about 10 cm. beyond the vertically positioned combustion furnace located directly above the column oven. A side arm was also sealed onto the column below the graded seal to serve as a solvent vent. The vent line was constructed to exit above the top of the oven and was sealed with a silicone plug when not in use.

The quartz tube extending above the top of the oven was enclosed in a Fisher microcombustion furnace (Catalog No. 20-288), which was operated at 950° C. for most of the work described. A Transite shield drilled to allow passage of the quartz tube was placed on top of the furnace to prevent the formation of cool spots in the reduction zone by a chimney effect. The furnace was clamped to a rod bolted to the side of the oven and could be swung out of the way for changing columns.

Reduction was carried out within the confines of an empty, narrow-bore quartz tube inserted into the larger quartz tube projecting from the reduction furnace, and connected to it with a tapered silicone plug. Dimensions of this tube are critical and appear to be optimum at 45-cm. by 3-mm. o.d. by 2-mm. i.d. under the conditions studied.

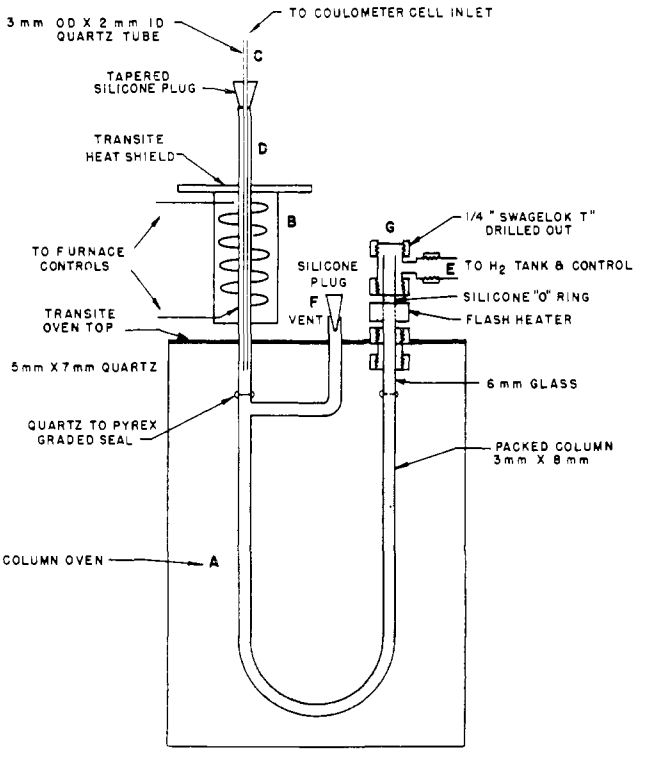

Figure 1. Schematic diagram of column oven and furnace

The tubes used for reduction had a fairly long life if kept clean. They can be detached from the apparatus and replaced in a matter of seconds. After five to seven runs they were cleaned by placing them in a muffle furnace at 600° to 700° C. for about one-half hour.

The exit of the reduction tube was connected to a length of $^1/_{16}$-inch o.d. Teflon tubing with a tapered plug which sealed the chromatographic column from the atmosphere. The Teflon tube led directly or through a secondary column into a microcoulometric titration cell. The cell inlet normally employed with the oxidation mode of analysis was not used. Instead, a medium glass frit (10-mm. o.d.) was inserted through the top opening of the cell and positioned just above the stir bar. The frit was connected with a silicone seal to the Teflon tubing leading to the reduction tube.

The subtraction unit used to remove H_2S and HCl consisted of a 7-cm. by 3-mm. i.d. glass tube packed with 6 cm. of Al_2O_3. The GSC column used to remove HCl while simultaneously resolving PH_3 and H_2S consisted of a 35-cm. by 5-mm. i.d. glass tube packed with 33 cm. of silica gel. These columns were inserted between the reduction tube and titration cell as required, and connected to them with $^1/_{16}$-inch i.d. Teflon tubing.

This prototype apparatus can be constructed from the components of many standard gas chromatographs. Subsequently, a factory-built oven was designed which contains several modifications to guard against hydrogen explosions. These include a purge line to prevent the buildup of hydrogen in the column oven, and a shutoff device which automatically interrupts the flow of carrier gas if the column pressure decreases below a preset value because of leakage. The apparatus described has been operated for more than a year and a half without these safety devices, and no explosions occurred. However, the inlet-column–reduction system consisted of a continuous length of glass sealed to quartz with no metal fittings or valves within the confines of the column oven.

Operation

The column oven, *A*, is adjusted to temperature, and the reduction furnace, *B*, adjusted to 950° C. A quartz reduction tube, *C*, is placed within the outer tube, *D*, and connected to it by a tapered silicone plug. The outlet of the reduction tube, *C*, is connected to the titration cell either directly, through the Al_2O_3 subtractor, or through the silica gel column. Carrier gas is introduced at *E* at a rate of about 15 ml. per minute. The sample in a few microliters of solvent is injected at *G* with the vent, *F* open. After the solvent has passed into the atmosphere, the vent is plugged to divert the gas flow through the tube, *C*, and thence into the titration cell. The microcoulometer and titration cell are operated in the usual manner except that a surfactant is used in the electrolyte, and the gases are introduced through a frit to ensure good dispersion.

The conditions for chromatography used in this work were as follows:

Chromatograph, Micro-Tek Instruments Co. GC 2500 with linear temperature programmer

Column dimensions, 1-meter × 3-mm. i.d. glass U-tube

Solid support, 80- to 90-mesh Anakrom

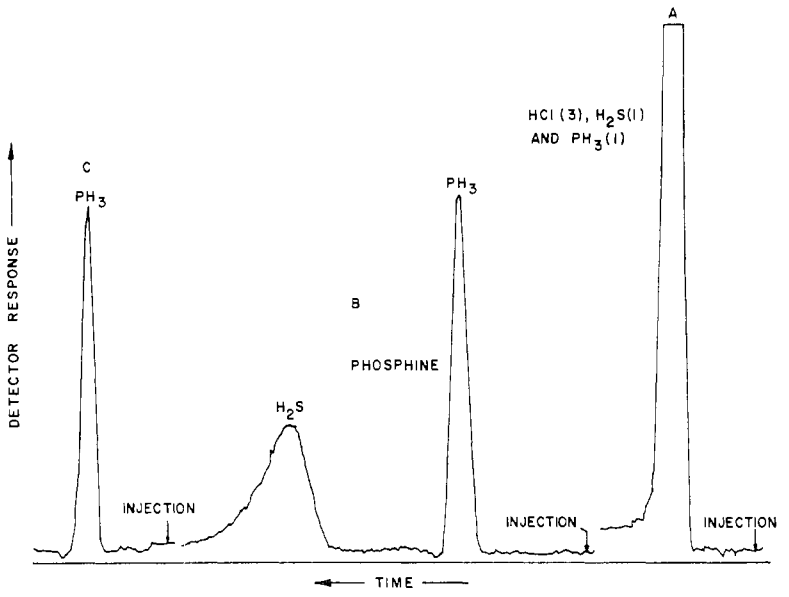

Figure 2. Chromatography of ronnel

A. With carrier gas passing directly into titration cell
B. With GSC column in place
C. With Al_2O_3 subtractor in place

ABS stationary phase, 10% DC 200, 12,500 CS silicone oil

Temperatures injection: 245° C. Column: 175°, 230° C. in 10 minutes, linear. Reduction tube: 950° C.

Carrier gas, hydrogen at 15 ml./min.

Detector, Dohrmann Instruments C-100 microcoulometer with T-200 halide cell

Recorder, Minneapolis-Honeywell −0.05 to +1.05 mv. operated at 1 inch per minute, 1 second full scale

Sample size, 0.5 to 5.0 μg. in 1 to 5 μl. of ethyl acetate or benzene

Retention time, up to 30 minutes.

Measurement of Reduction Products

H_2S and HCl are known to react with Ag^+ to yield Ag_2S and AgCl, respectively. However, the stoichiometry of the reactions of PH_3 with Ag^+ is less clearly defined. According to Van-Wazer (*6*), phosphides which may possibly contain unsubstituted hydrogen ($AgPH_2$, Ag_2PH, and Ag_3P) are formed from the reaction of PH_3 with solutions of metal salts. The results obtained in this investigation indicate that two equivalents of Ag^+ are precipitated per mole of phosphine, leading to the postulate that Ag_2PH is the primary reaction product. However, this could not be confirmed by polarography at concentrations of reactants several hundred times greater than are used in microcoulometry. Larger and variable quantities of PH_3 were removed from this system per equivalent of Ag^+, indicating that reactions leading to the formation of silver nitratophosphide, metallic silver, and various oxyacids of phosphorus were taking place. Phosphine will react with a large excess of silver salts in water to give a stoichiometric yield of phosphoric acid and metallic silver (*1*, *5*). Nevertheless, at the concentration ranges used for gas chromatography, the 2 to 1 ratio of PH_3 to Ag^+ approaches an integral number within experimental error.

However, the results obtained initially suggested that a smaller quantity of Ag^+ was being precipitated. This was caused by the low solubility of PH_3 in the electrolyte, which resulted in the escape of some of the gas into the atmosphere. This seems reasonable considering that the solubility of PH_3 in water is 27 ml. of gas per 100 ml. of solution. This explanation was confirmed by connecting two microcoulometer cells in series. Peaks were obtained from both cells on the injection of phosphine gas, and the ratio of the areas indicated that only about 30% of the phosphine injected was trapped in the first cell. The percentage of gas trapped increased with decreasing flow rate. Therefore, narrow (3-mm. i.d.) columns were selected for chromatography in order to reduce the volumetric flow rate to about 15 ml. per minute, while maintaining the linear flow rate in the customary range. This modification by itself did not solve the problem. When 0.2% Triton X-35 was added to the electrolyte to reduce gas-liquid interfacial tension, and the gas stream carrying the phosphine was intoduced into the cell through a frit positioned directly above the stir bar, these modifications led to the production of very small bubbles which were well dispersed in the electrolyte, giving the mixture a milky appearance. Under these conditions quantitative recoveries of PH_3 were obtained, and recoveries of H_2S and HCl were also satisfactory.

The initial objective of this program was to devise a procedure for the determination of organic phosphates, the measurement of chlorine and sulfur being only incidental. Therefore, a method was needed for removing HCl and H_2S from the gas stream without losing the phosphine. This was accomplished by inserting a short tube containing Al_2O_3 between the outlet of the reduction tube and the titration cell. This unit removes the HCl and H_2S quantitatively while permitting free passage of the phosphine. Peaks representing H_2S and HCl are never observed with this system, but after prolonged use the base line begins to increase because of saturation of the packing.

It is possible to measure PH_3 and H_2S selectively by inserting a GSC column containing silica gel between the reduction tube and titration cell. HCl is subtracted quantitatively, and PH_3 and H_2S are resolved. This GSC column works rather well for PH_3, but the H_2S peaks tend to broaden and increase in retention time as the column ages.

An illustration of the separations obtainable is shown in Figure 2. The peak shown in Figure 2*A* represents the sum of the cell response to HCl, H_2S, and PH_3 obtained on injecting the insecticide ronnel ($C_8H_8O_3SPCl_3$). The peaks obtained in Figure 2*B* were obtained when ronnel was injected into the chromatograph with a GSC column inserted between the reduction tube and titration cell. The first peak represents phosphine, and the second hydrogen sulfide. Although the peak profiles differ, their areas agree to within a few per cent of theory. The peak shown in Figure 2*C* was obtained when a subtraction tube containing Al_2O_3 was inserted between the reduction tube and cell. H_2S and HCl were removed completely, so that the peak observed could be due only to PH_3. AsH_3 and SbH_3 are the only possible interferences, and these are not likely to occur in the environments studied.

Contrary to general opinion, at low concentrations PH_3 is a very stable compound chemically, and is difficult to adsorb because of its low physical affinity for most substances. Column packings have not yet been found which subtract PH_3 while permitting free passage of HCl and H_2S. Efforts to remove phosphine by bubbling the gas stream through 50% trifluoroacetic acid and hydrogen peroxide solutions were unsuccessful. Phosphine is also more stable under the conditions used for reduction than was formerly believed.

Reduction of Pesticides

A variety of catalytic and noncatalytic packings were evaluated for use in the reduction step, but none of them gave completely satisfactory results. It was finally concluded that an empty quartz tube and a high reduction temperature yielded the best results. The dimensions of the tube are critical. Also, erratic results are obtained when its interior becomes coated with decomposition products. For this reason, a concentric design consisting of an inner and outer tube was employed for the reduction unit. Reduction takes place in the inner tube, which is easily removed and replaced. These tubes cost less than 50 cents each, and in any event can be cleaned for re-use by heating them in a muffle furnace. In initial work, the solvent was vented through the outer tube. This worked successfully for a time, but low yields of PH_3 were obtained after prolonged use because of the formation of carbon deposits on the wall, which resulted in poor heat transfer and lower temperatures in the reduction zone. This problem was solved by venting the solvent into the atmosphere before it entered the reduction zone. A vertical configuration for the reduction unit was adopted to allow for easy centering of the inner tube, and to prevent sagging of the quartz at the high temperature required.

The temperature range for optimum yield of PH_3 is 925° to 1000° C. The value of 950° C. used in this work was selected arbitrarily. Conversion efficiency falls off rapidly at temperatures below 900° C., and no PH_3 is obtained at temperatures below 700° C.

The product obtained on reducing organic phosphates in this apparatus has the same retention time on various stationary phases as pure phosphine, and displays the same low reactivity with most reagents. The microcoulometric cell response is also the same as that obtained with pure PH_3 after corrections are made for column losses during chromatography.

In view of the column losses incurred during the chromatography of most organic phosphates, and uncertainties concerning the stoichiometry of the cell reaction, it was necessary to assess the quantitative aspects of the method indirectly. Three methods were employed, and they all yielded substantially the same results.

In the first, a series of insecticides was selected which contained sulfur and phosphorus in various molar ratios. These were analyzed by the reduction method, first with the Al_2O_3 subtractor in the gas stream and then in its absence. By this means, it was possible to compare the cell response obtained with PH_3 and H_2S. Calculated area ratios were compared with observed ratios assuming that the compounds formed in the cell reaction were Ag_2S and Ag_2PH. Calculated and observed values compared favorably in most cases (Table I).

Table I. Responses Obtained with and without Alumina

Compound	Area Ratio Obsd.	Area Ratio Calcd.
Malathion 1P + 2S	2.9	3.0
Parathion 1P + 1S	2.0	2.0
Thimet 1P + 3S	4.6	4.0
EPN 1P + 1S	2.0	2.0
Diazinon 1P + 1S	2.0	2.0
Phosdrin 1P	1.1	1.0
Paraoxon 1P	0.97	1.0

A second method of evaluation was made possible by the observation that sulfur atoms bonded to phosphorus can be reduced to H_2S at 700° C., whereas the phosphate moiety does not yield PH_3 under these conditions. Thus parathion yields a response with the reduction furnace at 700° C., which is one half the area of the peak obtained at 950° C. Paraoxon does not yield a peak at 700° C., but at 950° C. a peak is observed which possesses an area one half that of the parathion peak. Essentially the same results were obtained on similar compounds. The results obtained on diazinon ($C_{12}H_{21}O_3N_2SP$) on reduction at 700° C., on reduction at 950° C. with the Al_2O_3 subtractor in place, and on reduction at 950° C. without the Al_2O_3 subtractor are illustrated in Figure 3.

Further confirmation was obtained by analyzing pesticides containing phosphorus and chlorine by both the oxidation and reduction methods. A Micro-Tek Model MT-220 gas chromatograph was used in the oxidation mode and the instrument described in this paper in the reduction mode. Column conditions were identical except for the nature of the carrier gas. The output from both systems was fed into the same titration cell. The results obtained are shown in Table II. Thus it appears that a 2:2:1 stoichiometry can be used with confidence in calculating results for PH_3, H_2S, and HCl, respectively.

Table II. Recoveries of Pesticides by Oxidation and Reduction Methods of Analysis

Compound	Recovery, % Oxidation (Cl^-)	Recovery, % Reduction (PH_3)
Trithion	73.6	70.0
VC 13	73.2	73.4
Ronnel	65.6	67.3

Chromatography

The results obtained on chromatographing a mixture of organic phosphate insecticides are shown in Figure 4. The effluent from the reduction tube was passed through an Al_2O_3 subtractor before entering into the titration cell, so that the peaks observed are due to phosphorus only. Standard column packings employed by the U. S. Food and Drug Administration for chlorinated hydrocarbons were employed (*2*). No work on column technology was done during this program, so that it is probable that the differences in peak areas which are observed were caused by decomposition of variable amounts of these compounds during chromatography.

To evaluate potential interferences in tissue extracts, samples of spinach were extracted and cleaned up by standard techniques employed by the U. S. Food and Drug Administration (*4*) and the extracts fortified with known amounts of organic phosphates. No peaks were observed which could be traced to natural products which survived the cleanup process. Recoveries of pesticides were equivalent to those obtained on standards. A large peak observed at 18 to 22 minutes in one series of experiments with fortified spinach extract was later traced to the presence of an organic phosphate in one of the solvents used during cleanup of the extract.

The specificity of the method for the organic phosphates is illustrated by Figures 5 and 6. Figure 5 is a gas chromatogram obtained on the extract of a urine sample of a patient on chlorpromazine ($C_{17}H_{19}N_2SCl$) therapy. It contains a large number of unresolved peaks due to chlorpromazine, chlorpromazine metabolites, and their thermal breakdown products. This chromatogram was obtained without the Al_2O_3 subtractor in place, so that the sum of chlorine, sulfur, and phosphorus is observed. Figure 6 is a chromatogram of the same sample using the Al_2O_3 subtractor. The high general background and peaks due to the presence of sulfur and chlorine compounds derived from the drug are eliminated, and a single peak representing a phosphorus-containing compound is observed.

Discussion

The reduction technique can be used to detect phosphorus compounds with almost absolute specificity, to measure sulfur and phosphorus independently when they are present in the same compound, or to measure the sum of chlorine, phosphorus, and sulfur. Ideally, it would be desirable to have subtractors available which would make it possible to measure each of these elements entirely independently. With the present system, the measurement of sulfur and phosphorus is difficult in complex mixtures owing to peak overlap, and the amount of chlorine in the sample must be measured by difference. Up to the present,

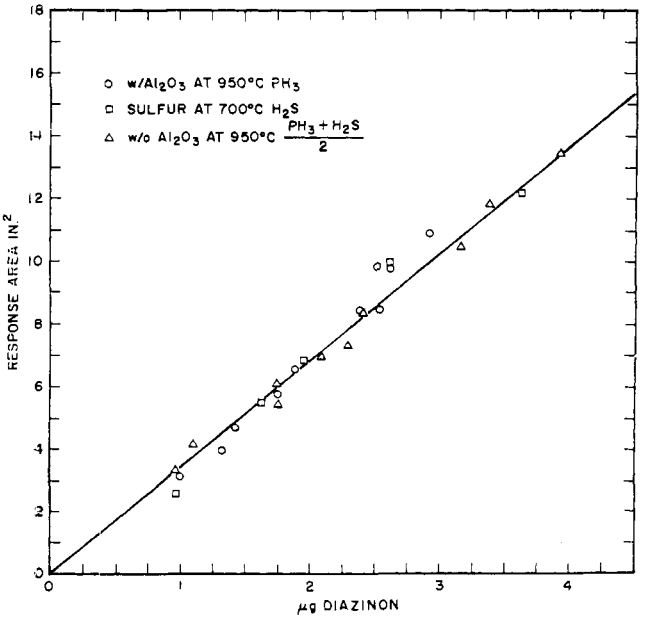

Figure 3. Determination of diazinon

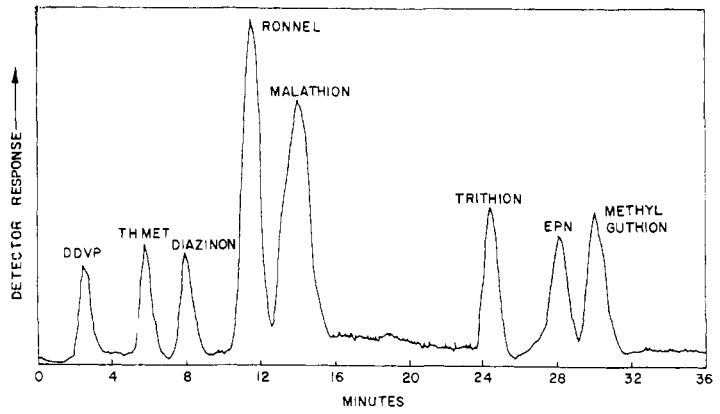

Figure 4. Chromatogram of mixture of organic phosphates with Al_2O_3 subtractor in place

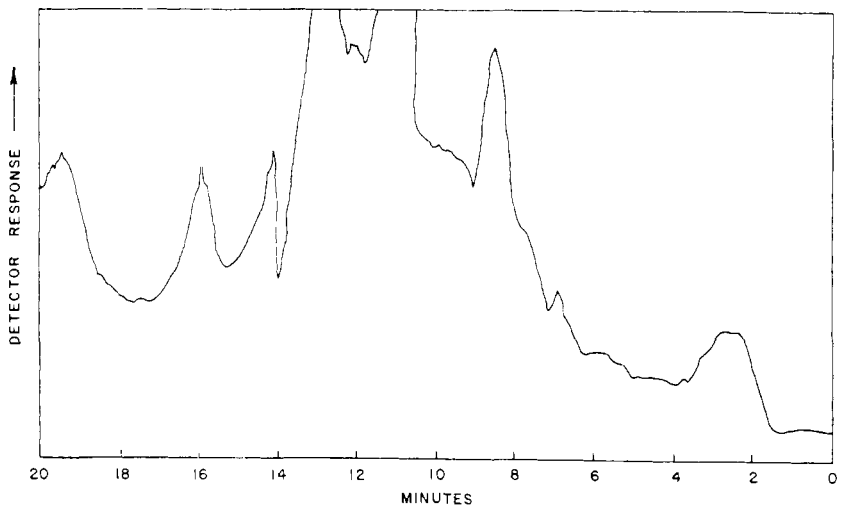

Figure 5. Chromatogram of chlorpromazine metabolites and decomposition products showing sum of Cl, S, and P

Table III. Theoretical Total Response of Various Pesticides Using Reduction Mode

Compound	Moles of Element Cl	S	P	Total Equivalents
Aldrin	6	0	0	6
DDT	5	0	0	5
2,4-D	2	0	0	2
Dieldrin	6	0	0	6
Heptachlor	7	0	0	7
Paraoxon	0	0	1	2
Parathion	0	1	1	4
Phosdrin	0	0	1	2
Ronnel	3	1	1	7
Thimet	0	2	1	6
Trithion	1	3	1	9

subtraction techniques have not been developed which result in the removal of PH_3 and permit free passage of H_2S and HCl.

However, independent measurements of the three elements can be achieved by employing the oxidation and reduction methods in parallel. The reduction mode provides for a direct measurement of phosphorus or a measurement of the sum of phosphorus, chlorine, and sulfur without use of a secondary gas chromatographic column. The oxidation system can be used to measure chlorine (halogen) with absolute specificity with Ag/Ag^+ titration cell. Sulfur can be measured independently by employing the I_2/I^- cell with the oxidation method. The possibility of measuring sulfur as H_2S with the Ag/Ag^+ cell and SO_2 with the I_2/I^- cell serves as a very useful crosscheck for confirming identity.

Moreover, preliminary work has shown that both phosphine and H_2S can be measured with the I_2/I^- cell, which would not be expected to measure HCl. The platinum electrodes of this cell must be gold plated in order to avoid the formation of a hydrogen half cell with the carrier gas. The quantitative aspects of this modification are still under investigation.

Useful information can also be obtained by running the reduction oven at various temperatures. All three elements of interest can be measured quantitatively at 950° C. for the compounds which have been investigated. At 700° C., compounds which contain phosphorus only do not yield responses. However, compounds which contain sulfur bonded to phosphorus atoms give quantitative yields of H_2S. When sulfur is bonded to carbon, the yields of H_2S obtained at 700° C. are low and variable. Thus it is possible to use this technique to obtain some insight into the nature of chemical bonding in pesticides as well as their elemental compositions.

The apparatus at present in use in these laboratories consists of a reduction oven

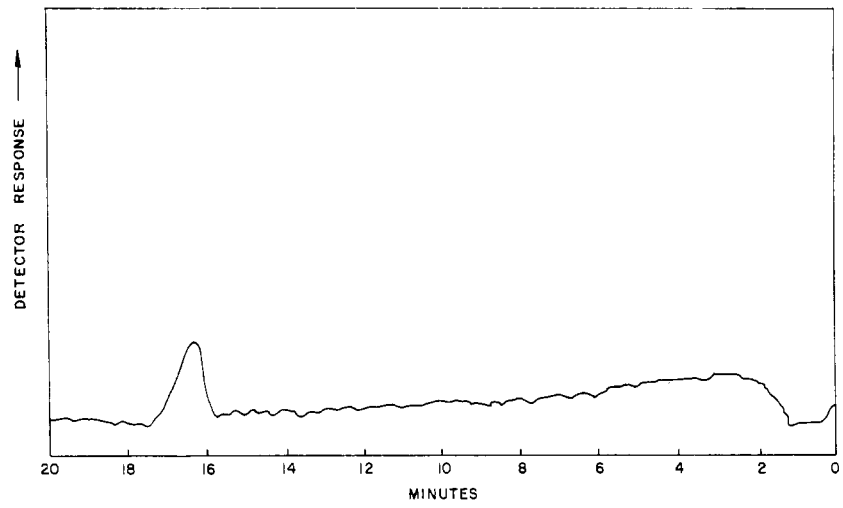

Figure 6. Chromatogram of chlorpromazine metabolites and decomposition products

and an oxidation oven, both feeding into the same titration cell. The cell may be of the Ag/Ag^+ type or the I_2/I^- type with gold-plated electrodes. Each oven contains two paired columns. One pair is packed with a nonpolar stationary liquid (silicone DC-200), and the second pair with a polar liquid (silicone QF—1+SE30). Thus it is possible to check retention times on both nonpolar and polar columns, and at the same time verify elemental composition by using the oxidation and reduction modes with either the silver or iodine cells. This combination affords excellent proof of identity in many cases.

The relative sensitivity of this method to various classes of pesticides when the sum of phosphorus, chlorine, and sulfur is measured is shown in Table III. Some of the organic phosphates such as ronnel and trithion yield responses equivalent to those obtained from chlorinated pesticides. Practical working sensitivity is of the order of 0.1 μg. for most compounds. With the Model C-200 microcoulometer it should be possible to obtain sensitivities substantially better than this. However, some modifications will probably have to be made for the measurement of PH_3 because of the changes in design of the titration cell, and the low solubility of this gas in the electrolyte.

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PHOSPHORESCENCE

Phosphorimetric Study of Some Common Pesticides

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The phosphorescence characteristics of 52 pesticides (including several known degradation products) are surveyed. Thirty-two of these phosphoresce sufficiently that excitation spectra, emission spectra, decay times, analytical curves, and limits of detection can be tabulated. The other 20 compounds did not give detectable phosphorescence excitation and emission spectra for 10^{-2} M ethanolic solutions.

As a preparation for work on crop residues of pesticides the application of phosphorimetry to the analysis of these residues was studied. Phosphorimetry has previously been used to determine the three major tobacco alkaloids (*6*), drugs in biological fluids (*5, 7, 8*), and air pollutants (*3*).

Experimental

Apparatus. All phosphorimetric measurements were taken with the Aminco Bowman spectrophotofluorometer (No. 4-8202) with the phosphoroscope attachment (No. C27-62140, American Instrument Co., Inc., Silver Spring, Md.). The mercury-xenon lamp (No. 416-993) was used for all quantitative measurements, while the xenon lamp (No. 416-992) was used to record all spectra. The quantitative measurements were made with the slit program: *A* 3 mm., *B* 4 mm., *C* 4 mm., *D* 3 mm., and *E* 3 mm., and the spectra with the slit program: *A* 3 mm., *B* 0.5 mm., *C* 0.5 mm., *D* 3 mm., and *E* 0.5 mm.

All spectra were recorded with a Moseley X-Y recorder (No. 135-A, F. L. Moseley Co., Pasadena, Calif.)

Reagents. All compounds were either analytical grade, obtained from major pesticide manufacturers, or technical grade, which had been redistilled or recrystallized until they appeared as one spot when chromatographed on a thin layer of silica gel. All compounds were stored at near 0° C. in a refrigerator before use.

Absolute ethanol (Union Carbide Corp.) purified as previously described