Phosphorus Detector for Pesticide Analysis

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A new detector for the gas chromatograph has been developed (4). It has the unique characteristic of being extremely sensitive to phosphorus containing compounds while simultaneously being insensitive to all other organic materials. These characteristics ideally suit the requirements for the analysis of phosphorus containing pesticides. This paper will describe the detector geometry, the operation and the performance characteristics including specificity, sensitivity, linearity and durability. Also included will be a demonstration of temperature program capability with the organo phosphorus pesticides.

Description of Geometry

The Aerograph Phosphorus Detector is basically very simple in design. A cross-sectional view of the detector assembly is shown in Figure 1. It consists of a standard hydrogen flame detector plus the addition of a small alkali metal salt pellet. Also added is a base extension for mounting purposes. The salt pellet consists of one gram of cesium bromide plus a suitable filler pressed under high pressure to form a rugged ceramic-like pellet. The base extension serves the dual function of repositioning the ignitor coil, when changing from the standard FID

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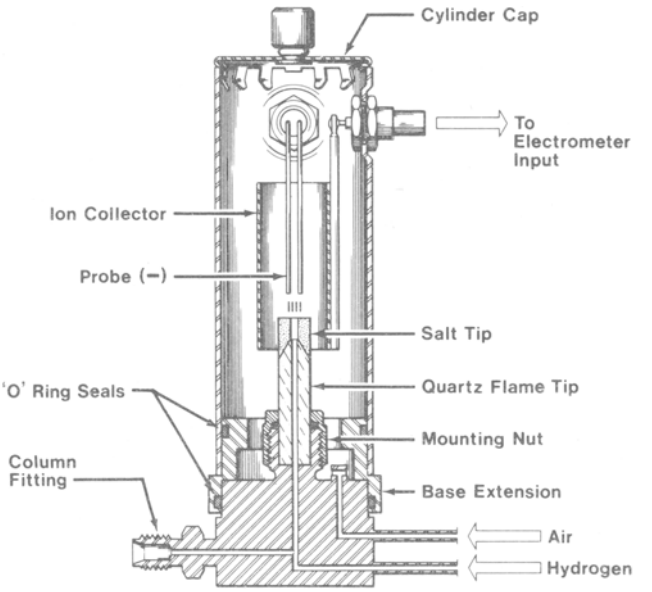


Figure 1 - Aerograph Phosphorus Detector

to Phosphorus Detector operation, and of sealing the base of the detector chamber from extraneous back-diffusion of air into the detector.

Operation

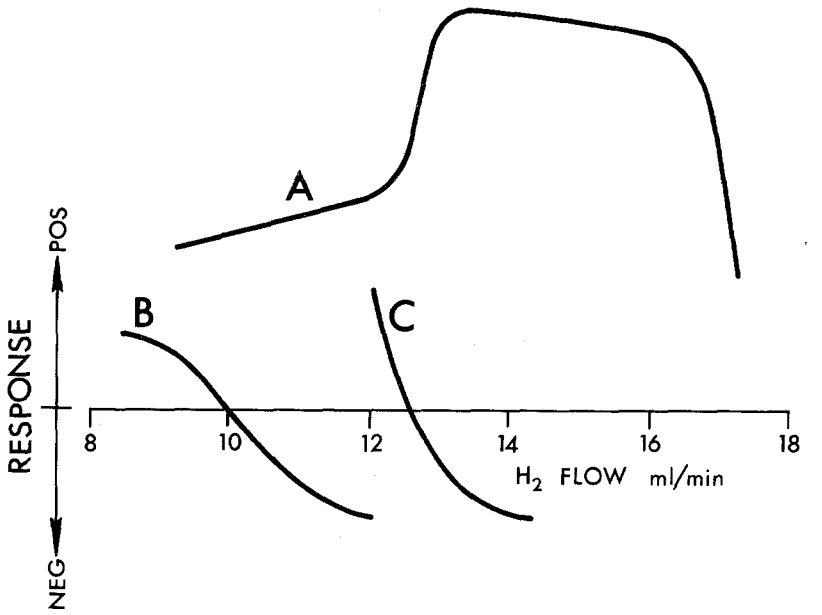
The operation of the Phosphorus Detector is much the same as the standard Flame Ionization Detector: a small hydrogen flame burns on top of the burner tip and ion products from combustion are collected. The similarity ends here as the standard FID uses a quartz burner tip and the Phosphorus Detector uses a cesium bromide burner tip. The background current of the FID is usually about 10^{-11} amps and the Phosphorus Detector is about 3×10^{-9} amps. As a matter of operating

procedure the H_2 flow is set so that this high background current is generated. This background current is generated by the ionization of the cesium bromide by the hydrogen flame. When a phosphorus-containing compound passes through the flame a further increase in collected ionization current is measured. The mechanism for this increased ionization is not known.

Flow Sensitivity - The detector has the undesirable characteristic of flow sensitivity. The air flow rate, required to support combustion and purge the detector chamber, requires control to $\pm$ 0.1 ml/min. of the 170 ml/min. used for normal operation. The hydrogen flow needs to be controlled to $\pm$ 0.01 ml/min. of the 14 ml/min. used for optimum performance. The absolute flow rate of H_2 or Air is not so important, but it must be carefully controlled. The flow control required for analytical purposes can be obtained with a high quality flow controller.

Performance Characteristics

Specificity - One of the unique characteristics of the Phosphorus Detector is that the detector approaches a classic ideal for a gas chromatographic detector in that it can be "tuned" to a particular class of compounds (4). Figure 2 demonstrates, qualitatively, the response of the detector to three different classes of compounds: phosphorus-containing (A), chlorine-containing (B), and normal hydrocarbons (C). As can be seen, the response to chlorinated compounds and normal hydrocarbons can be positive, zero, or negative depending on the particular hydrogen flow used. The response for phosphorus-containing compounds shows a sharp decline above 16 ml/min. because of the increased noise level associated with these flow rates. Although the peak height response increases, the noise level increases more rapidly to give a net decrease in minimum detectability.



A. Phosphorus Compounds
B. Chlorinated Compounds
C. Normal Hydrocarbon Compounds

Figure 2 - Selectivity of Phosphorus Detector

Sensitivity - Besides being ideally selective, the Phosphorus Detector more than adequately meets the sensitivity requirements normally imposed by pesticide residue analysis. Table I lists nine common organo phosphorus pesticides along with two figures for sensitivity to the Phosphorus Detector. The first column is the commonly used sensitivity expression gm/sec. which is determined by dividing the minimum detectable quantity in grams by the width of the peak in seconds. This sensitivity expression is an attempt to discount the fact that most compounds have different retention times. Since it is impractical to change conditions to elute every pesticide in the same time, the second column states the minimum detectability

in picograms using typical isothermal operating conditions. If these amounts were contained in one microliter of injected extract, they convert directly to ppb, i.e., 3 pg Thimet in one microliter equals 3 ppb minimum detectability.

TABLE I

Phosphorus Detector Sensitivity

Compound	Minimum Detectability gm/sec.	picograms	Retention Time Time (min.)
1 Thimet	$2x10^{-13}$	3	1.9
2 Di-Syston	$2x10^{-13}$	5	2.9
3 Methyl Parathion	$3x10^{-13}$	8	3.8
4 Parathion	$3x10^{-13}$	12	5.5
5 Malathion	$3x10^{-13}$	12	5.5
6 Ethion	$8x10^{-13}$	70	15.2
7 Trithion	$5x10^{-13}$	85	17.1
8 EPN	$4x10^{-13}$	100	26.7
9 Co-Ral	$7x10^{-13}$	500	69.8

Linearity - The typical range of linearity of the Phosphorus Detector is about 1000 fold. This refers to the range of concentration measured from minimum detectability to the highest concentration still yielding a proportional response to sample input. For example, the linear range of the pesticide parathion is from 10 picograms to 10 nanograms. This 10 nanogram upper limit of linearity does not mean that the detector ceases to function at higher concentrations, but that higher concentrations will yield a non-proportional response to increased sample load.

Durability - The most severe weakness of previously reported detector designs (1) (3) has been the poor reliability of the detector performance. The coated wire and screen required several hours to

equilibrate and suffered continuous sensitivity deterioration throughout its short lifetime. The Aerograph Phosphorus Detector, however, equilibrates in a matter of a few minutes, has an expected lifetime of thousands of hours, and maintains constant sensitivity throughout an 8-hour work day.

Experimental

The right-hand column of Table I would suggest that temperature programming might be used to good advantage to reduce the time of analysis and to improve the minimum detectability of Ethion, Trithion, EPN, and Co-Ral. Curve C of Figure 2 would suggest that temperature programming might be suggestful since the detector is insensitive to most materials normally associated with column bleed and temperature programming problems.

Apparatus - Figure 3 shows the front view of the gas chromatograph and flow control module used. The lower left module is the linear temperature programmer. The right-hand module is the dual differential electrometer (only channel "A" was used). Not shown at the back of the instrument is the separate detector oven with the protective detector insulator. Although this instrument can be used with dual column detectors, it has been used here with single column and single detector.

Conditions - The column used was a 5' x 1/8" Pyrex glass filled with 5% Dow-200 on Aeropak 30, 70/80 mesh. The temperature was programmed from 190°C to 250°C. The detector and injector temperatures were held isothermal at 200°C. The flow rates were 20 ml/min. nitrogen through the column, 170 ml/min. air to support combustion, and 14 ml/min. hydrogen. The pesticides were Thimet, Di-Syston, Methyl Parathion, Parathion, Trithion, Ethion, EPN, and Co-Ral. The

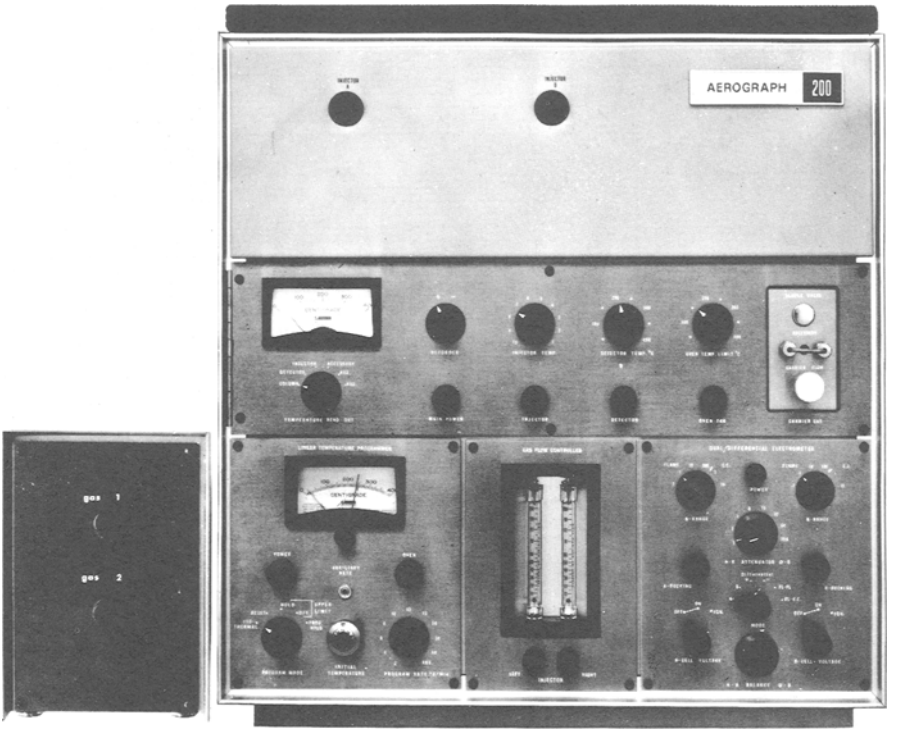


Figure 3 - Modular Analytic GC Ionization Detector - Dual Column

amount injected was 0.25 microliters of 2 ppm solution each, except 4 ppm EPN and 12 ppm Co-Ral. The attenuation is indicated on Figure 4 ($1x = 4 \times 10^{-10}$ amps full scale).

Results and Discussion

Figure 4 shows a typical temperature programmed pesticide analysis of the eight phosphorus-containing compounds. For this analysis to be done isothermally and achieve the same separation of early peaks would

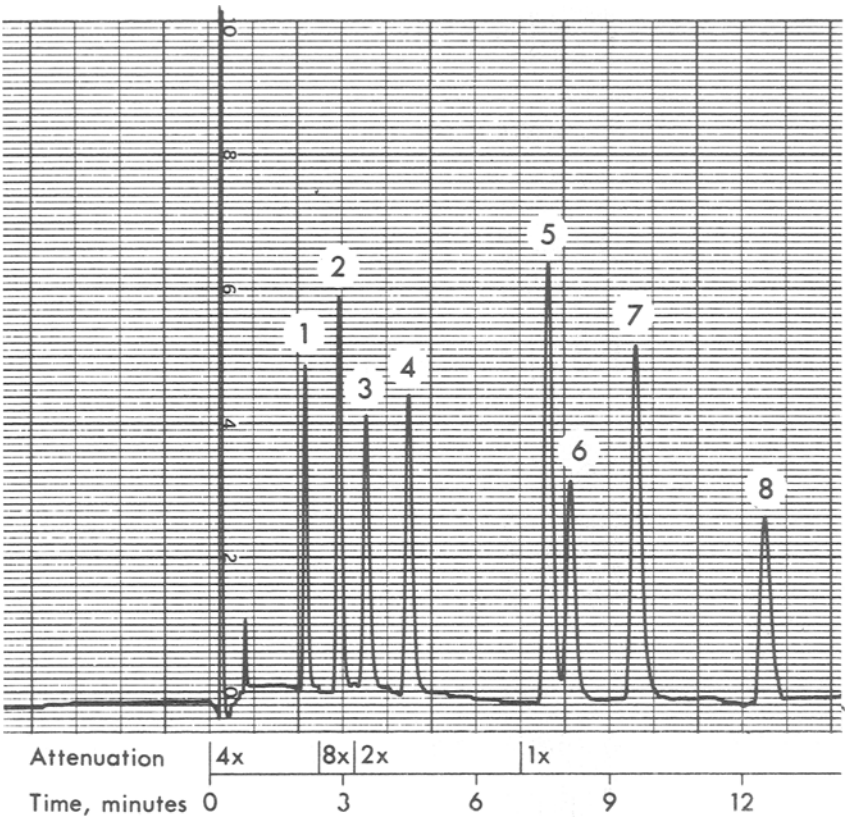


Figure 4 - Temperature Program of Phosphorus Pesticide

No.	Compound	Nanogram Amount
1	Thimet	0.5
2	Di-Syston	0.5
3	Methyl Parathion	0.5
4	Parathion	0.5
5	Trithion	0.5
6	Ethion	0.5
7	EPN	1.0
8	Co-Ral	3.0

Conditions

Column: 5'xl/8", 5% Dow-200
Column Temp: 190°C to 250°C
Injector Temp: 200°C
Detector Temp: 200°C
N_2 Flow: 20 ml/min.
H_2 Flow: 13 ml/min.
Air Flow: 170 ml/min.

require 71 minutes. The programmed analysis time was 13 minutes or 5-1/2 times faster. The accuracy of the temperature program is shown in Table II. The eight peaks are listed and their respective retention times given for 30 consecutive analyses. The relative standard deviation is calculated for each of the peak retention times and, as can be seen, represents high reliability for identification purposes. Previously the electron capture detector was the only detector capable of picogram detection of pesticides, but it could not be programmed because of its sensitivity to column bleed which changes with temperature. Although the Phosphorus Detector is only suitable for the analysis of phosphorus-containing compounds, at least this group is capable of this very useful gas chromatographic technique.

TABLE II

Peak No.	Compound	Average Retention Time (min.)	Relative Stnd. Dev.
1	Thimet	1.930	3.6%
2	Di-Syston	2.715	3.3%
3	Methyl Parathion	3.320	2.8%
4	Parathion	4.291	2.8%
5	Ethion	7.478	2.0%
6	Trithion	7.973	2.1%
7	EPN	9.475	2.0%
8	Co-Ral	12.225	7.8%

Besides improving the analysis time, programming increased the minimum detectability of the last three peaks 5, 5 and 3 fold respectively.

The Aerograph Phosphorus Detector has been used to demonstrate advanced techniques for residue analysis for phosphorus-containing compounds. The Phosphorus Detector now makes it possible to simul-

taneously analyze with two detectors - electron capture and phosphorus detector - this one group of pesticides by the powerful dual channel techniques (2). Dual channel chromatography of pesticides adds another dimension of quantitative and qualitative reliability for this analysis.

Acknowledgments

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