A Sodium Flame Detector of Increased Stability for Phosphorus-containing Pesticides[2]

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One of the chief difficulties in analytical gas chromatography is the identification of the resolved components of a mixture. The use of selective detectors sensitive to only a limited class of compounds can simplify this problem considerably.

Giuffrida and Karman have reported the development of such a detector (2,3,4), sensitive chiefly to compounds containing phosphorus and chlorine. A flame ionization detector is used, modified by placing a small amount of an alkali metal salt, usually a sodium salt, in such a position that it is heated by the flame. In some versions of this detector, one electrode is coated with the fused salt. In others, a probe containing the salt is placed in or near the flame.

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[2] Scientific Paper 2657, Washington Agricultural Experiment Stations. Work was conducted under Project 1793.

Bulletin of Environmental Contamination & Toxicology,
Vol. 1, No. 4, 1966, published by Springer-Verlag New York Inc.

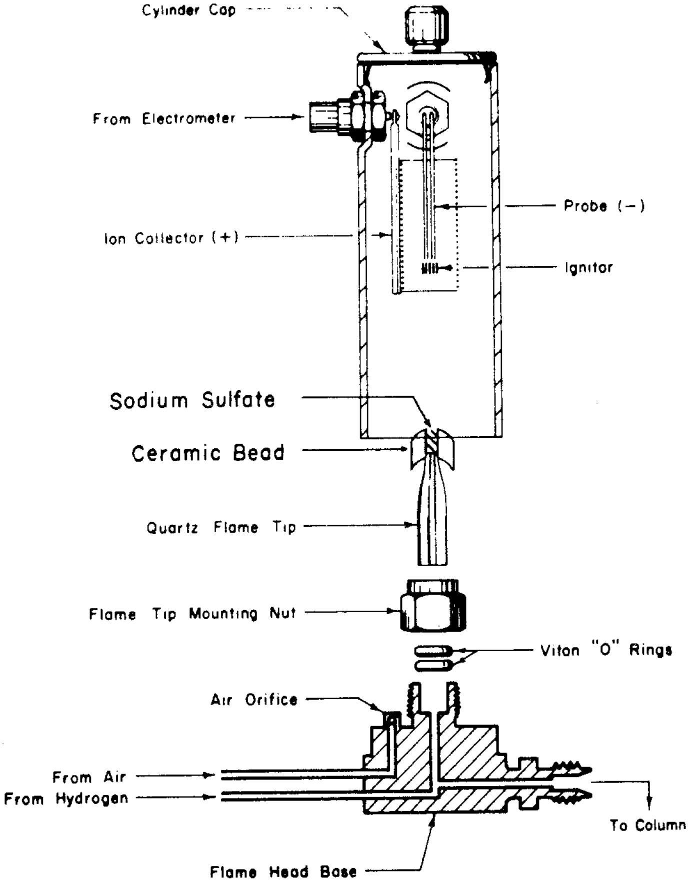

Figure 1. Construction of the sodium flame detector.

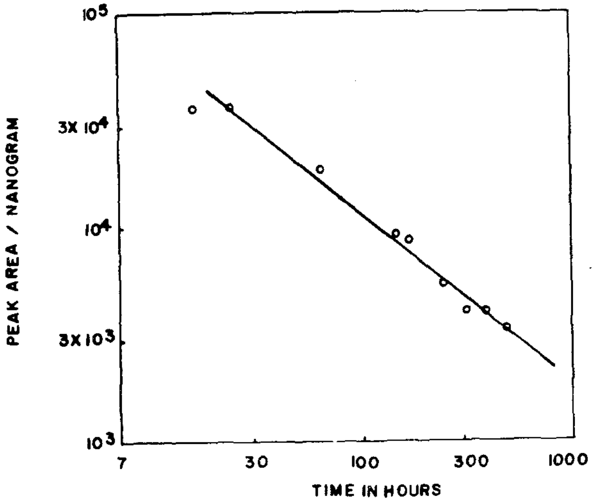

Figure 2. Detector response vs time.

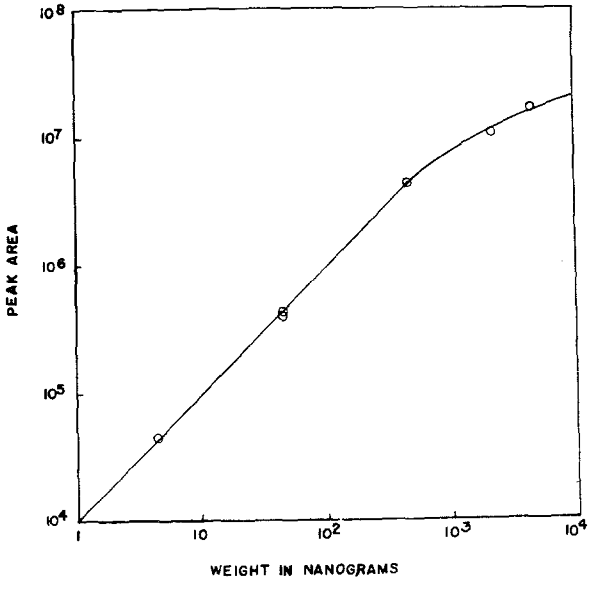

Figure 3. Detector response vs sample weight.

Several detector designs similar to those described by Karman and Giuffrida were tried with disappointing results. The thin salt coating was rapidly consumed, causing a large change in sensitivity within a few hours. Eventually we developed a much more stable s· stem, employing a modified Wilkens hydrogen flame detector. A ceramic tube[3] is placed around the jet (Figure 1). The cup so formed is filled with granular anhydrous sodium sulfate. The mixture of hydrogen, carrier gas and sample flows up through the salt bed and burns at its surface.

The response of this detector drops much more slowly than that of any other design yet tried by us. The detector can be used several weeks between fillings with salt granules (Figure 2). The rate of variation in response is comparable to that of an electron capture detector but is systematic instead of random. The limit of detection falls off less rapidly than the response, since baseline noise, as well as response, decreases with time. Figure 3 is a typical calibration curve. It can be seen that there is a thousand fold range of useable concentrations.

This detector has been compared with an unmodified Wilkens hydrogen flame detector for a representative group of compounds.

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[3] A ball and socket bead, #P189, inside diameter .29 cm. length .66 cm., manufactured by Saxonburg Ceramics, Saxonburg, Pennsylvania.

The results are shown in Table 1. A Wilkens Instrument and Research, Inc. Model A-600-C chromatograph with a 5' x 1/8" column of 5% Dow 11 on 60/80 mesh Chromosorb W was used. The carrier was Matheson prepurified nitrogen at 30 ml/minute. Hydrogen flow to the flame was 49 ml/minute. The column temperature was 188-190°C. All peaks were nearly symmetrical with very slight tailing.

TABLE 1

Comparative Response of Hydrogen and Sodium Flame Detectors

Weights and areas are the averages of several samples. Peak area is the product of peak height in recorder divisions at maximum electrometer sensitivity and width in seconds at half height. With the electrometer used, one division at maximum sensitivity represents 4.1×10^{-14} ampere, making a unit of area 4.1×10^{-14} coulomb.

Compound	Flame		Sodium Flame		Response Ratio
	wt, ng	area/ng	wt, ng	area/ng	
anthracene	74.4	26	21660	13	0.49
hexadecane	196	32	3737	15	0.48
ethyl stearate	1050	27	153000	5.2	0.19
Morestan	504	12	4490	71	5.8
aldrin	410	17	4044	1000	59
PCNB	345	9.2	3318	960	100
malathion	659	2.3	463	8600	3800
parathion	448	13	43	37,000	2800
Di-Syston	498	15	52	52,000	3400
Diazinon	280	24	26.7	75,000	3100
Phosphine			0.38	150,000	

As can be seen from Table 1, the ratios of the response of the sodium flame detector to those of the hydrogen flame detector fall into three groups. Compounds not containing phosphorus or chlorine have ratios near 1. The lower response per nanogram of the sodium flame detector to some of these materials may be due to the much greater sample size required. Compounds containing approximately 60% chlorine, such as aldrin and pentachloronitrobenzene (PCNB), give response ratios of about 100. Those containing about 10% phosphorus give ratios near 3000. Giuffrida and Karman have quoted various response ratios ranging up to 20 for chlorine and 600 for phosphorus compounds. It is evident that the cup type sodium flame detector has enhanced discrimination against phosphorus- and chlorine-free compounds, as well as improved stability.

To test the sensitivity of this detector to reduced phosphorus, an attempt was made to obtain the response ratio for phosphine. Although the sodium flame detector works well with phosphine, the response of the hydrogen flame detector is very erratic. It is suspected that the intrinsic sensitivity of a hydrogen flame detector to phosphine is very low, and that the observed response is due largely to contamination of the detector by traces of sodium salts, which are extremely difficult to remove.

Although both the baseline current and the noise level are much higher for the sodium flame detector than for the unaltered hydrogen flame detector, for organophosphates the smallest detectable quantity (that is, the limit of detection), is lower. The increase in noise is more than compensated for by the increase in Dimbat-Porter-Stross "sensitivity" (1). The increased baseline current may require a higher "bucking" current which can be obtained by increasing the voltage of the bucking battery or, in the case of a Wilkens electrometer, by setting the "range" switch to an "EC" position. (1) Baseline current, noise, and "sensitivity" all decrease slowly with time since replenishing the salt supply.

A typical noise level for the sodium flame detector is 1000 divisions at maximum electrometer sensitivity. The hydrogen flame detector sometimes gives a noise level as low as one division, but 20 to 50 divisions is not rare. Since the enhancement ratio for the phosphorus compounds tested is about 3000, the sodium flame detector has a limit of detection at least three times better than the hydrogen flame detector. Injections of four nanograms of Parathion or Malathion or of one nanogram of Diazinon or Di-Syston give clearly visible peaks. As can be seen from figure 3, the response curve is nearly linear up to several thousand nanograms.

We have used this detector for over a year in the analysis of soil and plant tissue samples for organophosphorus pesticides. Very few phosphorus-free compounds appear on chromatograms made with it and these can be easily identified as such by the use of a hydrogen flame detector. Its selectivity has made gas chromatographic analysis possible in some cases where plant materials previously interfered. In addition it often allows the use of simplified cleanup procedures, saving time and materials and giving improved recoveries.

References

1. M. Dimbat, P. E. Porter and F. H. Stross, Anal. Chem. 28, 290, (1956).
2. L. Giuffrida, Journal A.O.A.C. 47, 293, (1964).
3. A. Karman and L. Giuffrida, Nature 201, 1204, (1964).
4. A. Karman, Anal. Chem. 36, 1416, (1964).