The Characteristics and Operation Parameters of a Thermionic Emission Detector, Selective and Sensitive to Phosphorus

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The thermionic emission detector, a newcomer in the line of gas liquid chromatograph detectors, is rapidly proving to be a valuable tool for the specific detection of organophosphorus compounds. The greatest impact is presently in the pesticide field. At best, the detector is still plagued with some operational difficulties and detection inadequacies, leaving considerable room for its improvement. In addition, a complete theoretical description of the flame reaction mechanism is also still lacking. It is hoped that most, if not all of these difficulties can be overcome in the future as new research ideas are successfully applied. This paper is written to help the analyst, unfamiliar with the operations of a thermionic detector to avoid possible difficulties in its operation, as well as to stimulate new ideas to improve existing systems. For these reasons a literature review will be included.

1. Review

A hydrogen flame ionization detector for gas chromatography was first reported in 1958 by Harley, Nel, and Pretorius

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(1), and McWilliam and Dewar (2), the former describing a single flame system and the latter both single and dual flame systems. Since that time these detectors have been extensively used and are well known for their relatively high sensitivity to compounds capable of thermally generating carbion ions in the flame, and their lack of response to most other ionic species.

In March of 1964 Karmen and Giuffrida (3) reported a procedure for selectively increasing the responsiveness of a flame detector to compounds which contain chlorine, bromine, iodine, or phosphorus. A circular electrode coated with sodium hydroxide was suspended 5 mm above the flame and ninety volts were impressed between it and the body of the electrode. The resulting arrangement gave rise to an enhancement of the response to compounds containing halogens and phosphorus. In April of 1964, Giuffrida (4) described in detail the construction and optimal operation parameters of a similar specific detector, referred to as a Sodium Thermionic Detector. A coating of sodium sulfate was fused onto the electrode and a 300 volt battery was used to provide the detector voltage. The response on the thermionic detector to an organic halide was found to be greater than that of the conventional flame detector but considerably less than that produced by an organic phosphorus compound on the same thermionic detector. Some pesticide detection data was also included. In July of 1964, Karmen (5) reported a study of a single and a double flame thermionic detector. The single flame detector was constructed and operated similarly to those described previously. The double flame detector had two flame jets, one above the other with an alkali metal hydroxide or salt coated wire mesh screen between them. A particular advantage of the two-flame system noted was the complete insensitivity of the detector to non-phosphorus or non-halide containing organic compounds, once they had passed through the first flame. Near the end of 1964, Giuffrida and Ives (6) reported the use of a thermionic detector in an investigation of recovery procedures for several organophosphorus pesticide residues on various crops. The thermionic detector was used in conjunction with a flame ionization detector, the former providing quantitative pesticide recovery data and the latter providing cleanup efficiency data.

In June of 1965, three studies of interest involving the thermionic detector were reported. Coahran (7) converted a commercially available flame ionization detector to a thermionic detector by placing a ceramic tube over the flame tip and filling the "cup" thus formed with granular sodium sulfate. The emerging gases from the flame tip passed through the salt bed and burned on its surface. Greater long term stability was claimed for this system. Schmit, Wyme, and Peters (8) reported achieving good results by coating a copper electrode with a mixture of cuprous nitrate, boric acid, and acid silver solder flux. The electrode coil with its glassy coating was placed over the flame tip, and the remaining wire was attached to the lower end of the metal flame tip itself. The claims of the report were the development of a low noise, long life coating while preserving the sensitivity and specificity of the original detector. At this time our laboratory (9) reported the conversion of an existing flame ionization detector to a thermionic detector similar to Giuffrida's design (4). Contrary to some existing pessimism over the short-term stability of this detector design, it was found that with critical electrode placement and careful gas control, a system of comparable sensitivity and relatively long term stability could be devised.

In October of 1965, Karmen (10) reported a study involving the relative sensitivities of several halide and phosphorus containing organic compounds in the presence of interfering organic materials, in the double flame thermionic detector. Data on the comparison of several salt coatings were given with cesium chloride being found to be the most highly sensitive. In early 1966, Giuffrida, Ives and Bostwick (11) reported on an investigation of special ionization detectors which included operational parameters of their thermionic detectors. A study was made on several salt coatings, the results indicating that salts of potassium were of the greatest sensitivity. Thermionic and electron capture dual analysis data for several pesticides are also given.

Theoretical treatment of the flame mechanism of this unique detector is still lacking in the literature, to date. Padley, Page and Sugden (12), in their theoretical description of the mechanism of steady state ionization in flames, describe the special effect of halogens on the ionization in alkali-laden hydrogen flames. No similar treatment has been noted for phosphorus.

2. Experimental

The instrument used in this work is the Wilkens instrument and Research, Inc., Aerograph Hy-Fi Model 600 with flame ionization detector (FID).

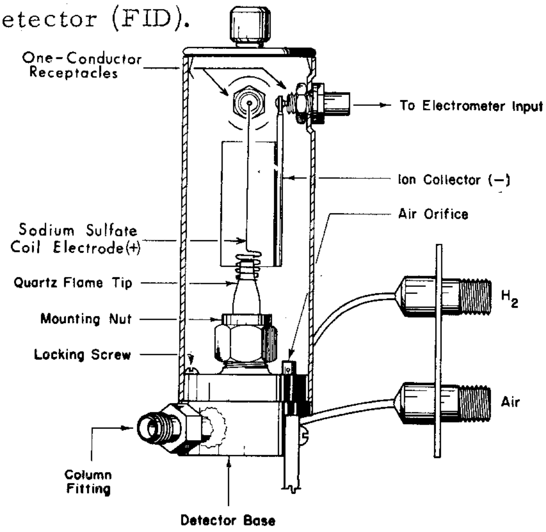

Figure 1.Sodium Thermionic Detector Head

The FID detector cell is converted to a sodium thermionic detector (STD) and is shown in Figure 1. Remove the two-conductor ignitor assembly from the FID cylinder and replace it with a one-conductor receptacle the same as that used to accommodate the ion collector. Make a five-turn coil out of nichrome or platinum wire, turning it on a 10-32 screw. Attach the wire to the newly-installed receptacle and center the coil 1-2 mm above the flame tip. Coat the coil with sodium sulfate[1] by successive applications of the saturated solution and warming over a low flame. It is convenient to remove the cylinder, leave the electrodes attached, and apply the salt solution with an eyedropper.

A standard one-conductor electron capture cell cable that contains the 470K resistor inside the cable plug connects the STD cell collector electrode to the 300v ionization output terminal of the instrument. This cable allows the cell to be operated at 90v which was found to be within the optimum voltage range for this system. The Wilkins Model 630 E. C. voltage control or equivalent is recommended where more exact voltage requirements are needed. Recent experiments have indicated that substituting a 90v "B" radio battery (+ to chassis ground) for the power supply will reduce the background noise somewhat at high sensitivity settings. A standard one-conductor FID cable connects the salt-coated electrode to the electrometer input terminal.

A large portion of the detector signal "noise" can be attributed to fluctuations in the H_2 gas flow to the flame. Therefore it is essential that some adequate means of gas regulation

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[1] We have recently found sodium or potassium borate to have better coating characteristics than the sulfate, with no decrease in sensitivity.

be included if high detector sensitivities are desired. A good, low pressure, precision regulator in series with a two-stage tank regulator functions well. It is also essential to include an indicating controller of the floating ball type or equivalent to insure reproducibility of flow rates. The Wilkins Model 650 hydrogen generator was found unsuitable for this application. The N_2 carrier gas flow seems to be sufficiently uniform and requires no special attention. Air flow was maintained as delivered from an aquarium pump and molecular sieve trap.

Operation of this detector is similar to a standard FID. Since the ignitor assembly was removed at the time of conversion, the H_2 is ignited with a flint striker. Carrier and H_2 flow rates should be 40 mls/min. and 50 mls./min. respectively. Attenuator settings are relatively high. A total signal attenuation of 32,000 x will produce a one-half scale recorder response to one microgram of parathion. Detection limits are one nanogram absolute minimum and approximately 10 nanograms being a workable limit.

3. Results and Discussion

The responses of the thermionic detector with different sodium salt electrodes at optimum hydrogen flow are shown in Figure 2. The numbers on the top of the bars refer to the relative hydrogen flow rates needed for maximum response. Although sodium chloride gave the highest response, it was found to be quite erratic at high sensitivities. The importance of hydrogen flow stability is self-evident in Figure 3. A small change in flow rate markedly affects the recorder response. In addition, the response of the phosphorus compound and that of the solvent are affected quite differently by the change in hydrogen flow, demonstrating the difference in the effect of the two substances on the alkali-laden flame. The cell voltage affects the response from the detector to 10 nanograms parathion as shown in Figure 4. Although higher sensitivities

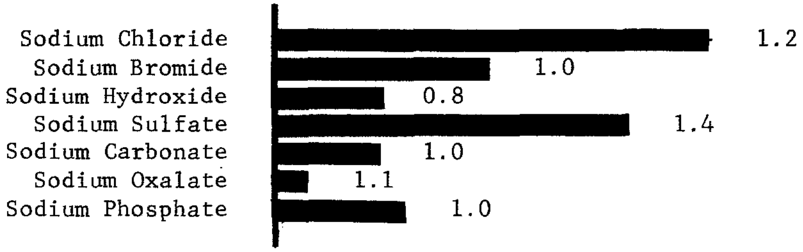

Figure 2. STD Electrode Salt Coating Response

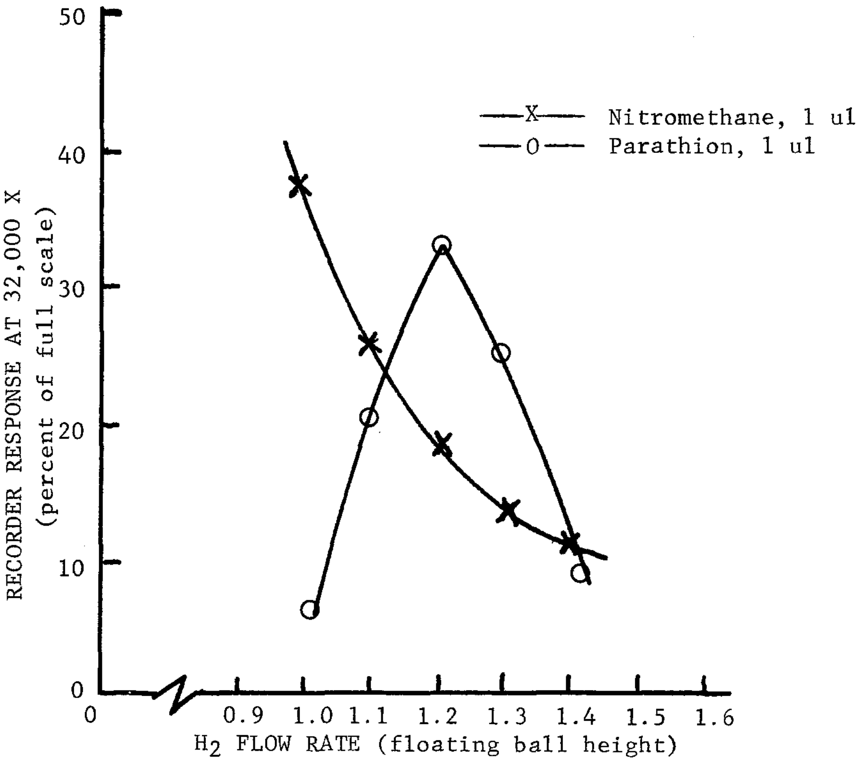

Figure 3. STD H_2 Flow Versus Response

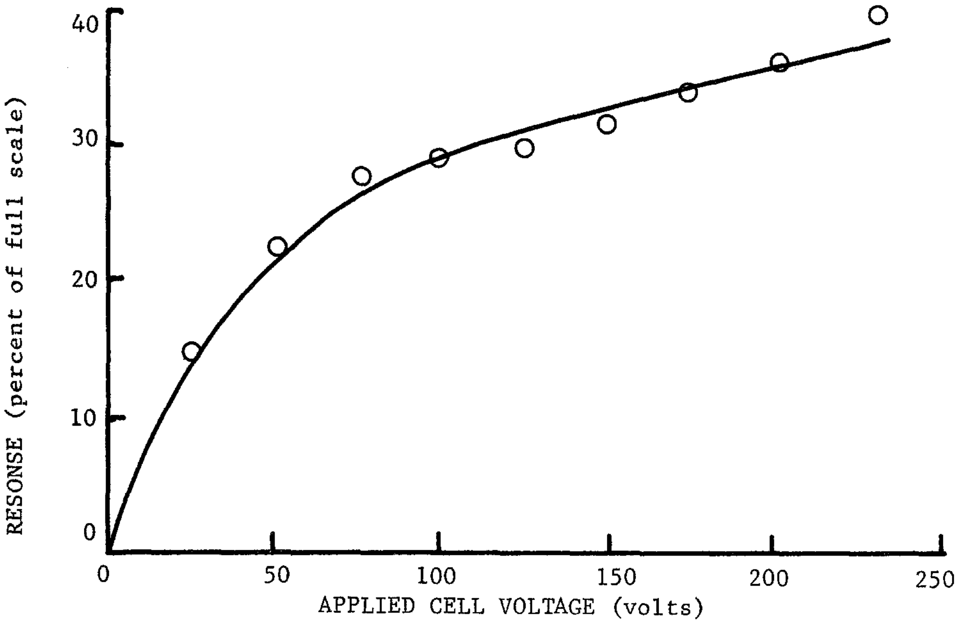

Figure 4. STD Response Versus Applied Voltage

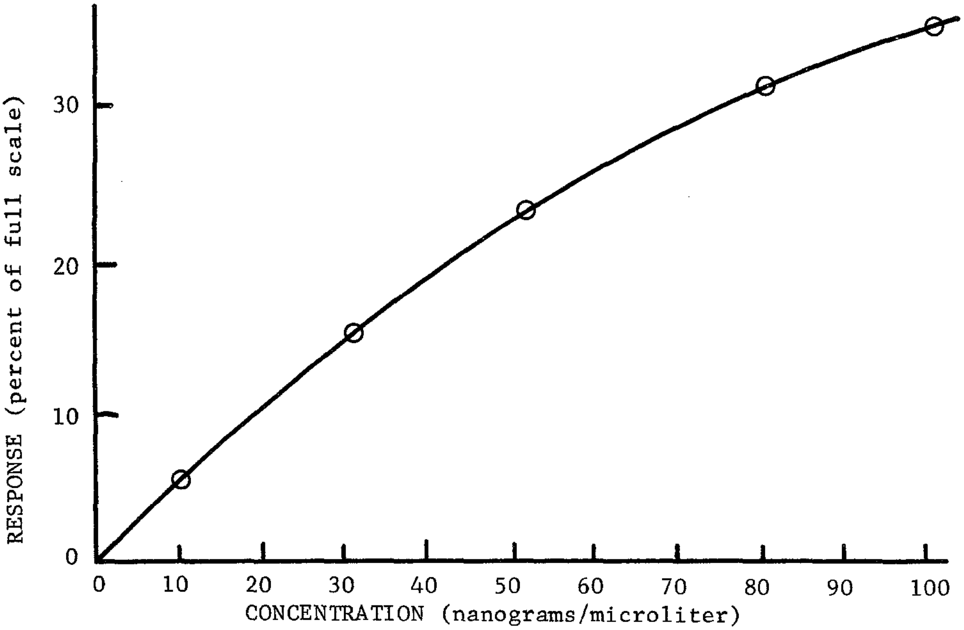

Figure 5. STD Response Versus Concentration

are achieved at higher voltages, the signal/noise ratio appears to improve in the direction of lower voltage. A concentration versus recorder response curve for parathion is shown in Figure 5. The curve is non-linear, indicating the need to plot a standard curve in quantitative analysis. A comparison of responses of several solvents on both the thermionic and flame ionization detector are shown in Figures 6 and 7. One microliter of each solvent was injected under the same column conditions. A one microgram parathion sample was also included. As indicated by this study the selection of a solvent for use with a thermionic detector differs considerably from that for use with flame ionization. Normally, where hexanes, benzene and similar solvents are not used with flame ionization detection, they work quite well with thermionic detection. The reverse is true for the chlorinated solvents.

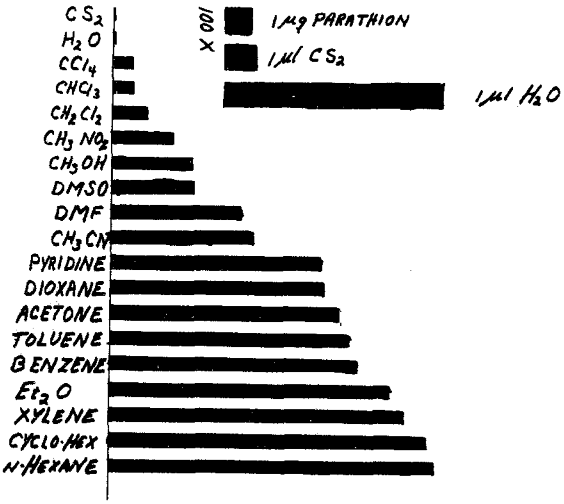

Figure 6. FID Solvent Response

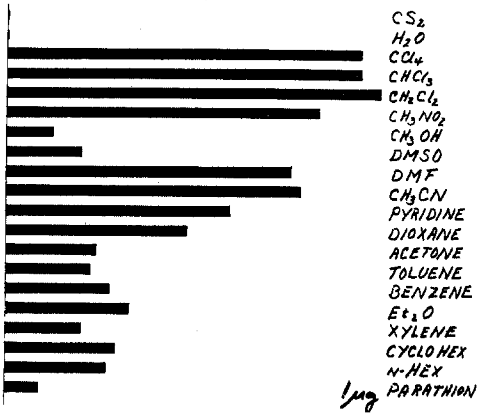

Figure 7. STD Solvent Response

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