

Determination of Insecticide Residue in Animal and Plant Tissues. V: A Device of Preparing the Specific Detector of Gas Chromatograph Highly Sensitive to Organophosphorus Insecticides. Yoshishige SATO, Junshi MIYAMOTO and Shin-ichi SUZUKI (Agricultural Chemicals Research Department, Osaka Works, Sumitomo Chemical Co., Ltd. Osaka) Received January 8, 1968. *Botyu-Kagaku*, 33, 8, 1968.

2. 動植物組織中における残留殺虫剤の定量 5. 有機りん化合物に特異的に高感度を示す熱イオン型水素焰イオン化検出器の試作 佐藤香重, 宮本純之, 鈴木信一 (住友化学工業株式会社 大阪製造所 農薬研究部) 43. 1. 8 受理

1964年 Giuffrida らによって Na_2SO_4 を用いた熱イオン型水素焰イオン化検出器がはじめて報告されて以来, ガスクロマトグラフによる有機りん農薬の残留成分分析の分野に各種の熱イオン型水素焰イオン化検出器が用いられて来た。それらの多くはいずれも使用寿命が短かくノイズレベルが高く長時間の連続分析に耐え得ないという欠点を有している。

著者らは, 上述の点を改良する目的で熱イオン源に KBr の単結晶の整形品を用いた熱イオン型水素焰イオン化検出器を試作した。この検出器は既存のものに比較して長時間の連続分析が可能であり, (連続使用時間は 100 時間以上であり, 整形しなおすことによりさらに 100 時間以上使用が可能であった) 雑音レベルが極めて低い。この検出器を用いて数種の有機りん殺虫剤の分析を行なったところ 1×10^{-11} グラムの最高感度を得, また 1×10^{-8} グラムの実用分析感度を得た。玄米, 野菜, 生ミルク等のサンプルについて残留分析を行ない 0.002ppm まで容易に分析することができた。

Introduction

The theory and mode of operation of the sodium thermionic detector (named STD) gas chromatography was first reported by Giuffrida (1964 a, b).

Recently in the residual analysis of organophosphorus compounds many workers have used the gas chromatograph equipped with STD and other specific detectors belonging to the same category, because the STD was found enormously sensitive to organophosphorus compounds and much less sensitive to other carbon compounds (Rahman 1965, Giuffrida 1966).

In the case of coiled wire-coated with sodium or other alkali metal salts, some difficulty was reported to happen, e.g. the average life time of the wire-shaped detector was only a few days at best.

Oaks (1966) devised such a type of detector with a considerably long durability by using pressed salt (cesium bromide) tip for salt reservoir. The present authors utilized a potassium bromide single crystal as salt source. This detector was named potassium thermionic detector, PTD, in this paper, which facilitated daily residue analysis, as compared with a previous wire coiled one (Miyamoto 1967), this type of PTD ensured long-

term operation with high reliability.

Experimental

a) Modification of the usual flame ionization detector to potassium thermionic detector.

The gas chromatograph of type GC-3AF, Shimadzu Seisakusho Co. Ltd., was utilized for the purpose.

Potassium bromide used for the measurement of IR spectra was cut by hand, as shown in Fig. 1, with a hole of ca. 0.2mm in diameter at the center. This crystal tip was mounted on the ceramic nozzle of FID and fixed. Fig. 2 shows schematically the PTD modified from conventional FID.

b) Operational condition.

As is well known, in working with such a specific type of detector, it is of utmost importance to control the hydrogen flow rate, because the magnitude of the base line current was closely related to the flow rate of hydrogen, as shown in Fig. 3, and that response to phosphorus compounds was dependent on the magnitude of the specific base line current, as reproduced in Fig. 4. That is, approximately 5.0×10^{-8} amp. maximum and 1.0×10^{-9} amp. minimum of base line current were found to be generated respectively at the hydrogen flow rate of ca. 45 ml/min.

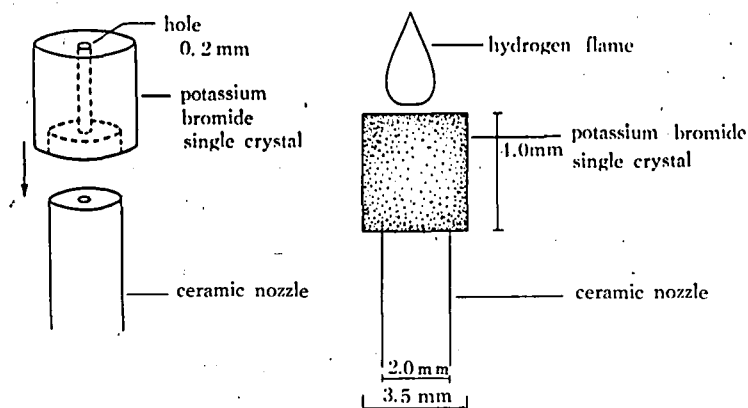


Fig. 1. An assembly of ceramic nozzle and potassium bromide single crystal.

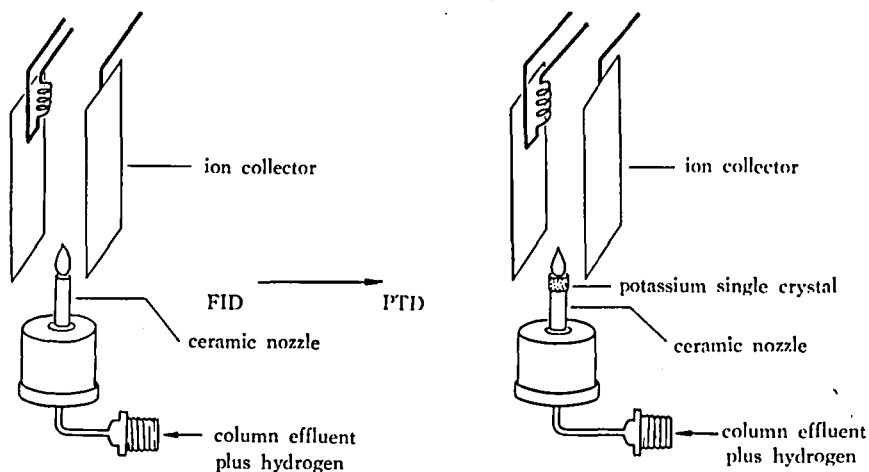


Fig. 2. A schematic drawing of the conversion of a flame ionization detector to a potassium thermionic detector.

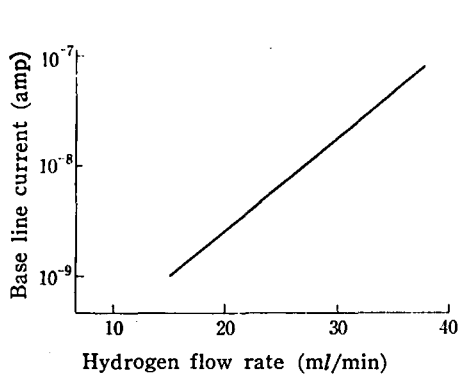


Fig. 3. Effect of hydrogen flow rate on PTD base line current.

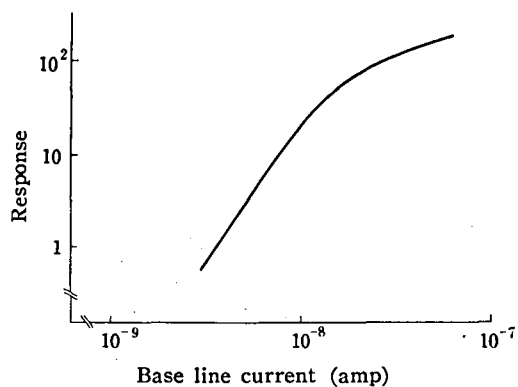


Fig. 4. Effect of base line current on detector sensitivity.

maximum and *ca.* 20 ml/min. minimum. The flame burning above the top of the salt tip generated a base line current some 200 times higher than the conventional flame detector. Under the actual operational conditions, hydrogen flow rate was so controlled as to obtain sensitivity giving 100 percent recorder scale response at 1.6×10^{-8} AFS, by injection of 10 nanograms of ethyl parathion. The sensitivity was 2,000 times greater at the maximum than that attained by the conventional flame detector. Under the same condition, other hydrocarbon compounds such

as BHC and dibutyl phthalate in the order of microgram were hardly detected, as evident in Fig. 5. Fig. 6 shows the response of PTD to 5 nanograms of methyl parathion, Sumithion® and ethyl parathion at the electrometer setting of 1.6×10^{-8} AFS. under 2.5×10^{-8} amp. base line current. Operational parameters in this case were as follows;

The pyrex glass column (on column injection system) $1.5M \times 4mm$ id., was packed with 1:1 mixture of 8% DC-200 and 16% QF-1 on 60~80 mesh chromosorb W aw. The carrier gas, helium, was adjusted to the inlet pressure of 2.0 kg/cm², *ca.* 40ml/min. Conditioning of this column was carried out at *ca.* 250°C for 24 hours with 50ml/min. helium flow rate. Thus, under the above conditions, this PTD gave noise-less, well balanced base line current and was highly sensitive to organophosphorus compounds. Moreover, it could be used satisfactorily for more than 100 hours, giving reliable, reproducible peaks.

c) Illustrative examples.

One hundred equivalent of tomato, cucumber or apple homogenates fortified with 10 micrograms each of methyl parathion, Sumithion® and ethyl parathion was processed as in the previous paper (Miyamoto 1967), except that *n*-hexane-acetonitrile clean-up step was omitted. One hundred grams of finely powdered rice grain were soaked together with 10 micrograms of the organophosphorus compounds in 200ml of benzene overnight. Benzene layer was separated by filtration and the filter cake was washed twice with 100ml each of benzene. After evaporation of the benzene solution *in vacuo*, the residue was partitioned between *n*-hexane and acetonitrile. Acetonitrile layer was separated and concentrated. After dissolved the residue in a known volume of acetone, an aliquot was gaschromatographed. Typical chromatograms of control and fortified samples are shown in Fig. 7. As evident from Fig. 7, peaks at the retention time of organophosphorus compounds were less than 0.002ppm equivalent. Organophosphorus compounds added to the homogenate were recovered substantially completely. Under the present experimental conditions, therefore, phosphorus containing insecticides present in samples at the concentration

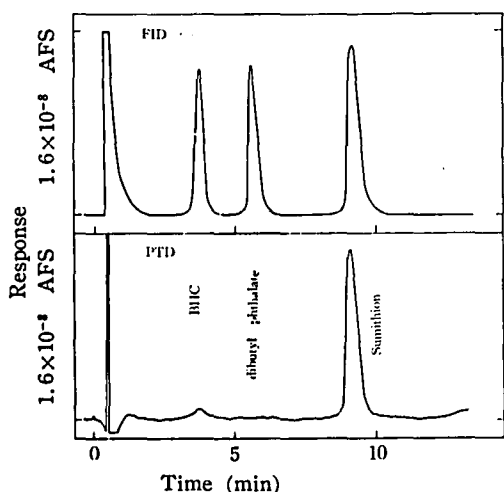


Fig. 5. Analysis of mixture of BHC, dibutyl phthalate and Sumithion by FID (upper) and PTD (lower). FID, BHC, dibutyl phthalate, Sumithion each 10 μ g. PTD, BHC, dibutyl phthalate, each 10 μ g, Sumithion, 5ng.

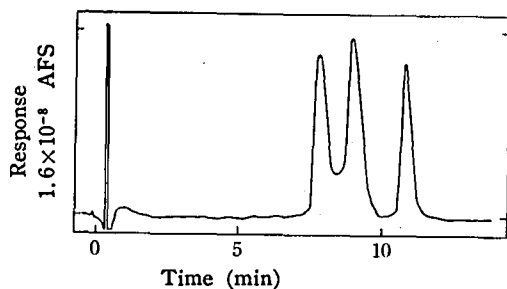


Fig. 6. Analysis of a mixture of 5 nanograms each of methyl parathion, Sumithion and ethyl parathion by PTD. (Curves, left to right; methyl parathion, Sumithion and ethyl parathion.)

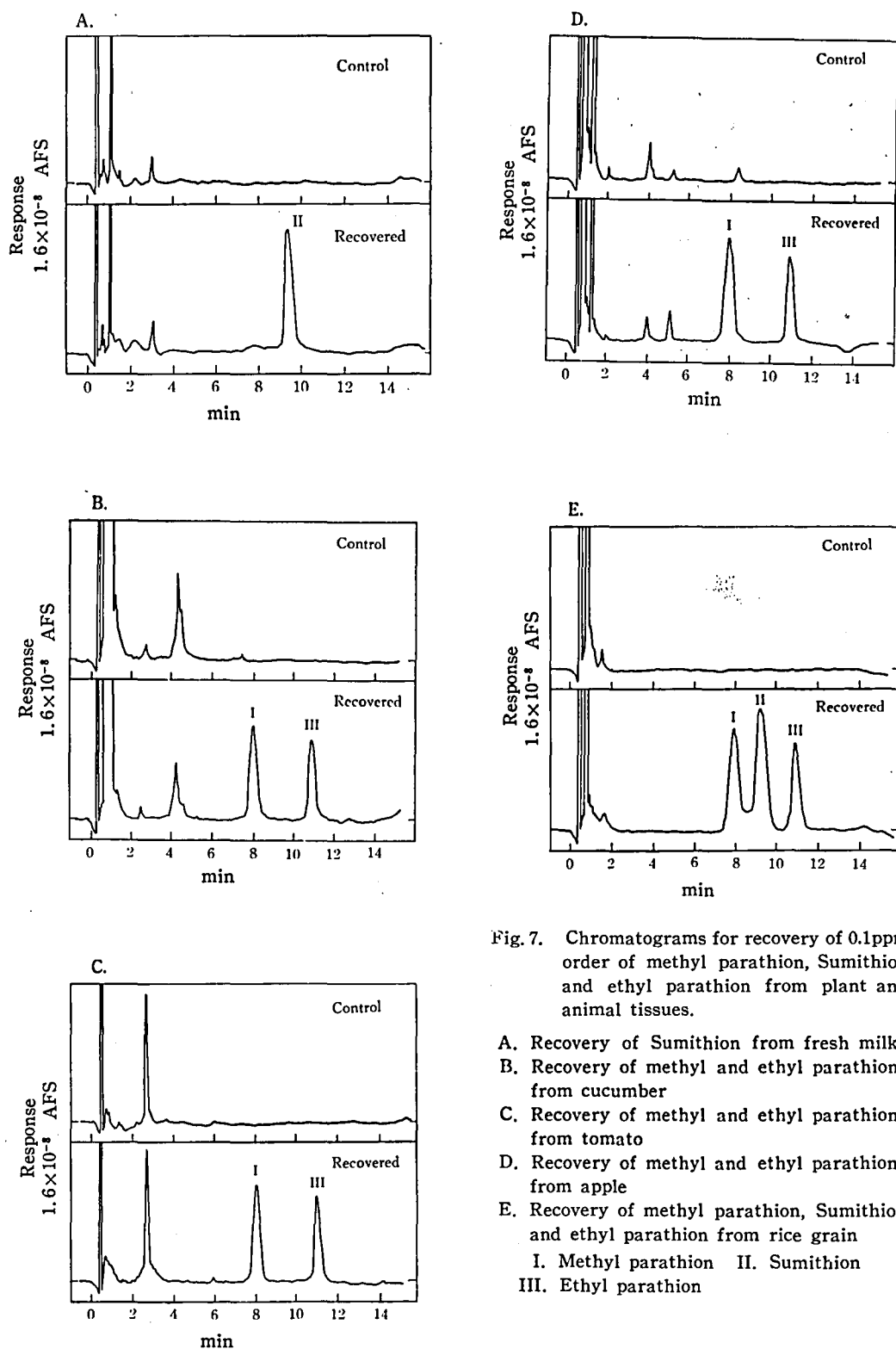


Fig. 7. Chromatograms for recovery of 0.1ppm order of methyl parathion, Sumithion and ethyl parathion from plant and animal tissues.

- A. Recovery of Sumithion from fresh milk
- B. Recovery of methyl and ethyl parathion from cucumber
- C. Recovery of methyl and ethyl parathion from tomato
- D. Recovery of methyl and ethyl parathion from apple
- E. Recovery of methyl parathion, Sumithion and ethyl parathion from rice grain
- I. Methyl parathion II. Sumithion
- III. Ethyl parathion

of above 0.002ppm can be determined.

Discussions

Compared with PTD reported here, the previous coiled wire STD (Miyamoto 1967) was of far shorter durability and gave less reproducible peaks. Moreover, this STD required far longer pre-conditioning period before use. These unfavorable properties of the STD are seemingly due, for example, to the fact that the distance between spiral and burning flame is varied, and that alkali metal salt layer is not always uniformly coated, which makes ion temperature unstable. The PTD is free from such unfavorable factors and ion temperature is presumably solely dependent on the hydrogen flow rate, giving rise to the stable sensitivity to phosphorus containing compounds. Furthermore, potassium bromide single crystal contains minimum amount of impurities, which favors also to gain stable base line current; powdered potassium bromide of guaranteed reagent grade compressed to a tablet could not be used practically because of noises often generated.

As shown above, PTD required much lower hydrogen flow rate for a given base line current than coiled STD (Oaks 1966, Itaya 1966). Although it has not yet been certain that this enhanced base line current in itself results directly in the higher sensitivity to phosphorus, for the sensitivity rather depends on the temperature of potassium ion emitted (Itaya 1966), the increased base line current greatly affects the sensitivity. Therefore, it was found necessary to control flow rate of hydrogen very strictly, which was attained sometimes only with difficulty with such a type of apparatus.

When a potassium bromide tip was mounted on one of the dual detector nozzles and gas-chromatograph was run, much more amount of base line current was generated on PTD side,

and it was difficult to adjust the recorder. Thus, the operation could not be done at the hydrogen flow rate of more than 30ml/min. (above 2.8×10^{-8} amp. of base line current). This difficulty was overcome by introducing a selector switch between mercurial batteries (by doubling the capacity of battery, if necessary,) in the feed-back circuit of electrometer, to counter-balance the enhanced base line current, and as the results the sensitivity was increased further by more than ten times.

Thus, the potassium thermionic detector developed here can be effectively used, as shown in Fig. 7, for the microdetermination of organophosphorus compounds in animal and plant tissues. Indeed, combined with suitable extraction and clean-up procedures, the residue less than 0.01 ppm could be very easily measured gaschromatographically with the modified detector.

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Literatures Cited

- Giuffrida, L.: *Jour. of A. O. A. C.*, 47, 293 (1964a).
 Giuffrida, L. and F. Ives: *ibid.*, 47, 1112 (1964b).
 Giuffrida, L., F. Ives and D. Bostwick: *ibid.*, 49, 8 (1966).
 Itaya, M.: Speech at The 15th Joint Annual Meeting of the Japan Society for Analytical Chemistry (Fukuoka) (1966).
 Miyamoto, J., Y. Sato and S. Suzuki: *Botyukagaku*, 32, 95 (1967).
 Oaks, D. M., K. P. Dimick and H. Hartmann: Varian Aerograph reprint No. 122 (1966).
 Rahman, A. and A. E. Refai: *Jour. of A. O. A. C.*, 48, 374 (1965).