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HIGHLY STABLE AND SENSITIVE THERMAEROSOL DETECTOR FOR THE ANALYSIS OF PHOSPHORUS- AND NITROGEN-CONTAINING COMPOUNDS

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SUMMARY

Modifications to thermionic detectors have some limitations associated with a considerable dependence of the sensitivity and reproducibility of the detector operation on the flow-rate of hydrogen, air and carrier gas, rapid exhaustion of the alkali metal salt source and the difficulty of replacing one salt by another. The proposed thermaerosol detector makes it possible to avoid these limitations. The characteristics of the detector and examples of its application to the analysis of pesticides are presented.

In the thermionic detector (TID), which is widely used in gas chromatography, the injection of the vapour of an alkali metal salt into a hydrogen flame results in a thermionic effect in the form of a large increase in the sensitivity of detection towards certain groups of organic compounds, for instance, phosphorus- and nitrogen-containing compounds[1].

In the well known modifications of the detector, the vapour of the alkali metal salt is injected into the operating volume of a flame-ionization detector, from the salt which is heated either by the flame or by indirect heating by an electric current.

Studies of the mechanism of operation of the detector[2,3] have shown that the main processes occur in the flame and the salt serves only as a source of alkali metal atoms.

The drawbacks of such detectors are as follows: the gas flow-rate has a large influence on the main characteristics of the detector; it is difficult to replace the salt reservoir; the source of the alkali metal vapour is rapidly exhausted, with a consequent short time of continuous operation of the detector without changes to its main characteristics; and contamination of the salt by the products of combustion of the substances being analysed. The last drawback leads to instability of the detector operation.

The stability of the hydrogen flow-rate in the TID must not be worse than $\pm 0.1\%$, and the carrier gas flow-rate $\pm 0.5\%$. Maintaining the flow-rates of the

carrier gas and hydrogen with such accuracy is difficult, especially with automatic chromatographs.

In order to overcome the above drawbacks and to take account of a number of conclusions concerning the mechanism of operation of the detector, a highly stable thermionic detector, named the thermaerosol detector (TAD)[*], has been developed. In this detector, the detector operating volume is separated from the site of formation of alkali metal salt vapour. A schematic diagram and the circuitry for the supply and measurement of TAD signals are shown in Fig. 1.
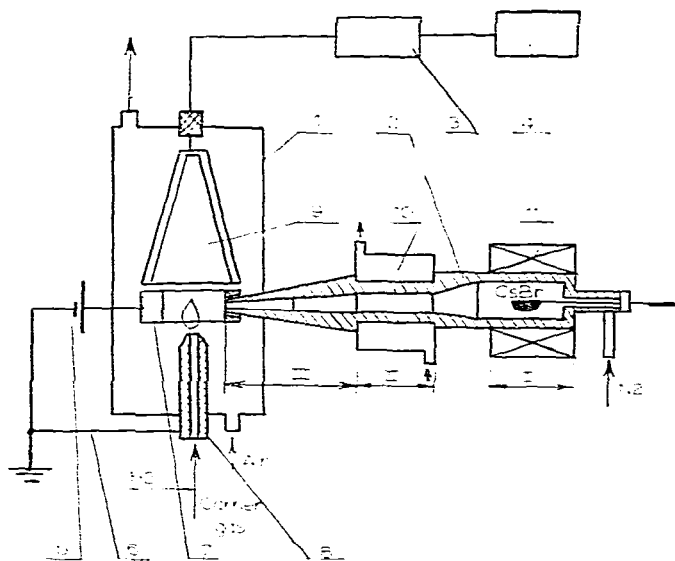

Fig. 1. Schematic diagram and circuitry of TAD detector. 1 = Flame-ionization detector; 2 = aerosol generator; 3 = electrometric amplifier; 4 = recorder; 5 = voltage supply source; 6 = detector burner earthing; 7 = potential electrode; 8 = burner; 9 = measuring electrode; 10 = refrigerator; 11 = thermostat. I = evaporation zone; II = zone of aerosol formation; III = nozzle.

The detector is a combination of a conventional flame-ionization detector (1) with a generator of an aerosol of alkali metal salt (2). The aerosol generator consists of three parts: a thermostat oven for evaporation of the alkali metal salt from the reservoir in the flow of an inert gas necessary for transporting the vapour of the salt into the detector flame: a cooled zone for converting the salt vapour into mono-disperse aerosol particles: and a cone-shaped nozzle for the injection of the aerosol into the flame zone.

The size, materials and location of the aerosol generator with respect to the flame-ionization detector are chosen so as to prevent the decay and coagulation of the aerosol particles before their introduction into the flame. A positive voltage of 100–300 V is applied to the potential electrode of the detector (7): the burner (8) and the negative pole of the voltage supply source are earthed. The signal from the measuring electrode (9) is applied to the input of an electrometric amplifier (3) and recorded by a potentiometer (4). The circuit of the voltage supply shown in Fig. 1 makes it possible to obtain a low noise level and more stable characteristics

of the detector. As the source of alkali metal vapour, caesium bromide was used, located in a quartz holder (5).

The pumping in of salts in the form of aerosol particles provides a more stable flow of alkali metal than in a conventional TID. Aerosol particles of the salt are introduced into the hot zone of the detector (inside the potential electrode) and are carried away by the air flow to the outlet of the detector. At the exit (in the cooled zone) some condensation of the salt takes place, but this does not affect the operation of the detector.

The alkali metal salt is evaporated in a thermostat cell, the temperature of which is maintained to within $\pm 0.1°$ with the aid of a proportional thermoregulator. The salt heating temperature is about $500°$. The inert gas flow transfers the vapour formed into the cooled part and, when subjected to a large temperature gradient, the salt vapour changes into a state of oversaturation and then into an aerosol. Monodispersion of the aerosol is achieved by diluting it with a large flow of inert gas.

The detector can be operated for more than 2000 h without the need to replace the salt reservoir, the sensitivity and background current being maintained. An experiment involving weighing the salt was carried out. Evaporation of the salt after 22 h of continuous operation amounted to 0.4 mg. Hence the efficiency of the aerosol generation is about $1.8 \cdot 10^{-5}$ g/h. The amount of caesium bromide placed on the quartz holder was about 1.0 g. The size of the aerosol particles, measured with the help of filters with an electron microscope, was 0.1–1 μm, 80 % being particles of size 0.1 μm.

The dimensions of the generator and the gas flow-rate are chosen so as to prevent coagulation of the aerosol particles during their transport into the detector operating volume.

Before placing the salt in the generator, it is heated for 20–30 h at $400°$ in order to remove volatile contaminants that would increase the noise level and drift of the detector.

A marked advantage of the proposed TAD design is an insignificant dependence of its sensitivity, baseline drift and noise level on the gas flow-rates (hydrogen, air and carrier gases) over a wide range. For instance, the sentitivity of the TAD changes by only 1 % on changing the hydrogen flow-rate by 1 %; the dependence of the sensitivity on changes in the carrier gas (nitrogen) flow-rate is even lower, being 0.4 % per 1 % change in flow-rate.

The relationships between the detector sensitivity and gas flow-rates (Fig. 2) show that the sensitivity remains virtually unchanged when the hydrogen flow-rate changes from 23 to 37 ml/min and that of air from 215 to 360 ml/min. Such relationships result in a high stability of the detector operation and reproducibility of the readings.

The characteristics of the detector are given in Tables I and II. The TAD has characteristics similar to those of various TIDs[5–12].

There are wide possibilities for the optimal operation of the detector in analysing different groups of compounds and for the optimal choice of the carrier gas flow-rate in order to obtain the greatest efficiency of separation.

The response of the detector was measured after its continuous operation for 2 months when the flow of aerosol particles was turned off. The response of the
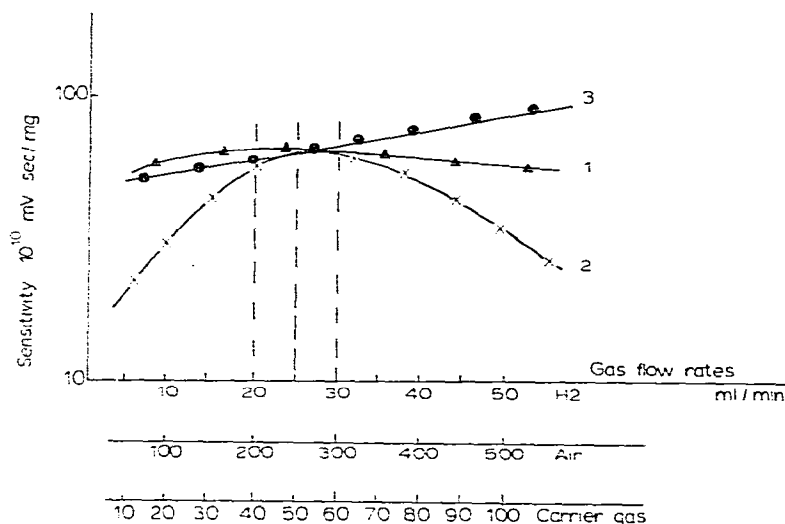
Fig. 2. Relationships between TAD sensitivity and flow-rates of hydrogen (1), air (2) and carrier gas (3). Salt, CsBr; supply voltage, 300 V; salt temperature, 500°; detector temperature: 200°; temperature of the zone being cooled, 20°; gas (N_2) flow-rate for injecting aerosol into the detector, 260 ml/min. The relationships were obtained by changing the flow-rate of one gas when the optimal flow-rates of the others were hold constant.

detector to methylparathion was reduced by several orders of magnitude and became approximately the same as that of a normal flame-ionization detector.

With its high stability of operating characteristics, the TAD has a high sensitivity and selectivity towards organic compounds containing phosphorus or nitrogen, and it was for such compounds that it was designed. For example, the minimal detectable amount (expressed as the element) when analysing phosphorus-containing compounds is *ca.* $2.5 \cdot 10^{-14}$ g/sec and when analysing nitrogen-containing compounds *ca.* $5 \cdot 10^{-13}$ g/sec. Such a high sensitivity indicates possibility of using the detector in devices for environmental control in analysing the threshold limit concentrations of organic substances.

TABLE I

CHARACTERISTICS OF COMMERCIAL TAD

Chromatograph	Crystal 4001
Optimal gas flow-rates (ml/min)	
H_2	25
Air	250
N_2	20–40
Make-up (N_2)	260
Potential (V)	300
Salt	CsBr
Equilibration time (min)	20
Continuous operation time (h)	>2000
Linearity	10^4
Detection limit (g/sec)	$2 \cdot 10^{-13}$
Test compound	Metaphos (methyl parathion)

TABLE II

CHARACTERISTICS OF TAD

| Substance	Atom	Sensitivity		Selectivity (g X^*/g C)	Efficiency of ionization
		Coulomb/g	Coulomb/g X^*		
Rogor	P	0.62	4.6	$0.85 \cdot 10^5$	$1.5 \cdot 10^{-3}$
Methaphos (methyl parathion)	P	1.04	8.8	$1.6 \cdot 10^5$	$2.8 \cdot 10^{-3}$
Methylnitrophos	P	1.2	10.8	$2.0 \cdot 10^5$	$3.5 \cdot 10^{-3}$
Carbophos	P	0.45	4.8	$0.9 \cdot 10^5$	$1.5 \cdot 10^{-3}$
Phtalophos	P	0.43	4.4	$0.8 \cdot 10^5$	$1.4 \cdot 10^{-3}$
Fosalon	P	0.5	5.9	$1.1 \cdot 10^5$	$1.9 \cdot 10^{-3}$
Propasin	N	0.1	0.33	$0.06 \cdot 10^5$	$2.4 \cdot 10^{-3}$
Hexane	C	$4.5 \cdot 10^{-5}$	$5.4 \cdot 10^{-5}$	1.0	$4.0 \cdot 10^{-8}$

* X = Element being determined.
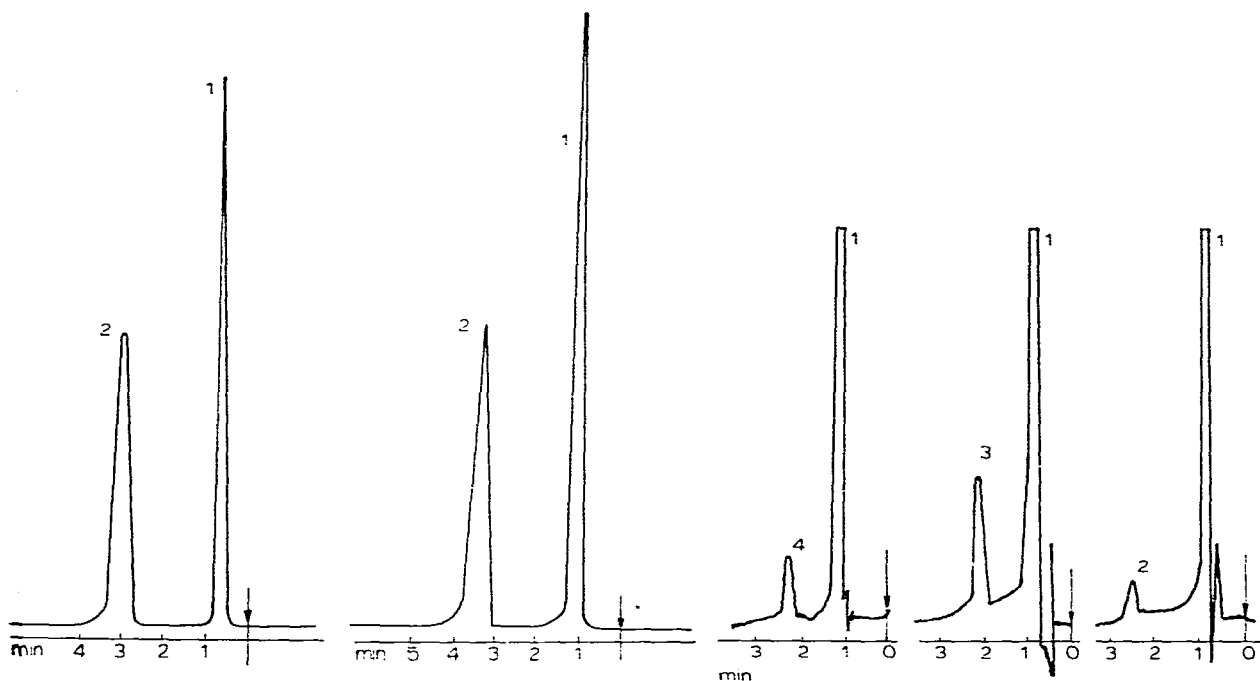
Fig. 3. Chromatogram of a phosphorus-containing organic compound. Peaks: 1 = solvent (n-hexane); 2 = methyl parathion (metaphos), $0.9 \cdot 10^{-3}$ mg/ml in a sample (ca. 1 ng). Temperatures: column, 190°; detector, 200°; generator, 500°. Flow-rates: hydrogen, 24 ml/min; carrier gas, 21 ml/min; air, 260 ml/min; nitrogen, 260 ml/min. Salt, CsBr; detector voltage, 300 V; sample size, 1 μl. Column: glass, 1 m × 3 mm I.D., 5% SE-30 on Chromaton (0.2–0.3 mm).

Fig. 4. Chromatogram of a nitrogen-containing compound. Peaks: 1 = solvent (n-hexane); 2 = prometrin, $1 \cdot 10^{-2}$ mg/ml in a sample (ca. 10 ng). Conditions as in Fig. 3.

Fig. 5. Chromatogram of several pesticide contamints in surface waters at the threshold limit concentrations obtained with a Crystal 4001 chromatograph. Peaks: 1 = n-hexane; 2 = carbophos (malathion) (0.05 mg/l); 3 = Metaphos (methyl parathion) (0.02 mg/l); 4 = Phtalophos (imidane) (0.19 mg/l); Conditions of the analysis and sample volume as in Fig. 3.

The TAD thus designed could be used in automatic systems for controlling the contamination of surface waters, determining the amounts of phosphorus- and nitrogen-containing organic impurities at the threshold limit concentrations.

The important advantages of the new detector are the simplicity of its design, the possibility of rapid replacement of the salt without dismantling the detector and the stability of its operation for a long period (several thousand hours) without the need to replace the salt reservoir.

Chromatograms of several phosphorus- and nitrogen-containing organic compounds are presented in Figs. 3–5.

The TAD is commercially available in the Crystal 4001 gas chromatograph (Ministry of Instrumentation of the U.S.S.R., Moscow, U.S.S.R.), which also has flame-ionization and electron-capture detectors, and is used for environmental protection purposes.

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