CHROM. 9098

THERMIONIC IONIZATION DETECTOR FOR THE ANALYSIS OF PHOSPHORUS- AND NITROGEN-CONTAINING ORGANIC COMPOUNDS

V. V. BRAZHNIKOV and E. B. SHMIDEL

Gas Chromatography Centre, Mosneftekip str. 1, Moscow (U.S.S.R.)

SUMMARY

The mechanism of the selective sensitivity of the thermionic ionization detector has not previously been elucidated, despite a number of interesting designs and improved characteristics of thermionic detection techniques. In this paper, a probable mechanism of the processes that occur in the detector is proposed. An explanation is given of the generation of signals from phosphorus- or nitrogen-containing organic compounds and a detector with improved characteristics is described.

INTRODUCTION

The thermionic ionization detector (TID) for the analysis of phosphorus- and nitrogen-containing organic compounds was proposed in 1964[1]. Since then, various designs of the detector and investigations of its characteristics have been published. The detector has become widely used in chromatography, along with katharometer, the flame ionization detector (FID) and the electron-capture detector[2], and is commonly employed in the analysis of compounds that contain phosphorus, nitrogen and halogens. However, the basic physical principles of operation of this detector have not been elucidated and the detection mechanism is not yet clear in many respects.

A review of the literature on the TID up to 1970 was published by Brazhnikov *et al.*[3]. They drew attention to the increasing fields of application of the detector, but pointed out a number of contradictory and vague data obtained with it. In that review, three possible mechanisms of the processes that occur in the detector were discussed, but none of them gave a complete explanation of its characteristics and its high sensitivity to some compounds and no conclusion was drawn as to which of these mechanisms might be the most likely.

The first mechanism, associated with the phenomena of surface ionization and positive thermionic emission, is typical of detectors that operate according to the principle of a halogen-leak detector[4].

The second mechanism suggested that when atoms of an alkali metal collide with H_3O^+, CHO^+ and other ions formed in the flame, they are easily ionized (the detector background current) and intermediate products of the reaction of organic phosphorus-containing compounds (PH_2, PO, PO_2) form phosphorus ions in the

flame, which transfer the charge to additional amounts of alkali metal atoms (the detector signal).

The third mechanism suggested was associated with the phenomenon of photo-evaporation of salt from the surface of a salt reservoir owing to the radiation of photons formed during the combustion of organophosphorus compounds in the flame.

Some work has been carried out[5] aimed at obtaining some additional quantitative data about the detector. The results of this work indicated that the main process occurs in the working region of the flame and not on the surface of the salt; the salt serves only as a store of alkali metal atoms; and the rate of evaporation of the salt from the surface of the salt reservoir is not changed when phosphorus-containing compounds enter the detector. It was concluded that further development of the detector to establish optimal operating conditions and to ensure its wide application was impossible without a thorough understanding of the physical principles of the operation of the detector.

Scolnik[6] attempted to explain the detection mechanism on the basis of tests on a flameless ionization detector, which was called a "chemiionization" detector (CID). He came to the conclusion that ionization takes place in the gas phase and that the presence of hydrogen has nothing to do with the operation of the detector (the processes in which hydrogen participates do not play the major role in the detection mechanism). The results showed unambiguously that the ionization current depends on the concentration of alkali metal vapour.

Consideration of the operation of the Pye Unicam three-electrode detector[7] and the Perkin-Elmer detector with a salt ball at a negative potential[8] has made it possible to conclude that the zones of the signal formation from organic solvents and from phosphorus-containing compounds are spatially separated and the zone of the formation of the latter is near the collector electrode. Some detector designs have been described in which the alkali metal salt was not in the flame region and was evaporated with the aid of additional heating[9] or was injected in the flame as an aerosol[10].

For these detectors, the dependence of the detector background current and sensitivity on the flow-rate of hydrogen is smaller. In addition, the insertion of the collector electrode into the hotter flame zone reduced the sensitivity of the detector to phosphorus-containing compounds.

Ševčík[10] explained the TID mechanism and different anomalies in the operation of the detector using data from previous publications. He ascertained that heat energy is the source of ionization, and that the measured signal current is generated by a number of processes, the greatest contribution being made by the ionization of atoms of the alkali metal. Ševčik's opinion was that the detection mechanism is associated with the formation of specific compounds that contain heteroatoms. In this paper, we suggest a mechanism of TID operation based on the assumption that near the surface of the collector electrode, aerosol salt particles are formed which are in equilibrium with the vapours of salts of alkali metals that surround them.

DETECTION MECHANISM

With the aim of achieving a proper understanding of the processes that occur in the flame while detecting compounds that contain heteroatoms (P or N), it is necessary to consider two main problems: energy aspects of flame ionization and the

mechanism of ion formation. Numerous experimental data from the literature and those obtained by ourselves show that essential processes in the TID do not occur on the salt surface but in the volume of the flame, where the reaction of the vapours of alkali metal salts with hydrogen is thermodynamically possible, resulting in the formation of alkali metal atoms, *e.g.*:

$$CsBr + H \rightleftharpoons Cs + HBr \tag{1}$$

The following discussion concerns the case when the salt CsBr is used in the TID. However, it is applicable to any other alkali metal salt when analyzing phosphorus- and nitrogen-containing compounds.

As the temperature near the surface of the collector electrode decreases sharply (Fig. 1a), the formation of aerosol alkali metal particles may occur in this zone. The atoms of Cs form ions and electrons due to ionization in the hydrogen flame. Although the ionization potential of Cs is 3.88 eV (which exceeds the energy of the hydrogen flame in the presence of the alkali metal salt), Cs ions can be formed by means of the following mechanism. The Cs atoms excited in the flame during the transition from the excited state into the ground state emit γ quanta:

$$Cs^* \rightarrow Cs + h\nu \tag{2}$$

When the number of Cs atoms is sufficient, γ quanta are absorbed by other Cs atoms and the number of the excited atoms in the hydrogen flame does not decrease because of light emission[11]. Cs ions are formed as a result of the collisions of the excited atoms of Cs with other atoms:

$$Cs^* \rightarrow Cs^+ + e^- \tag{3}$$

One can assert that the main component of the background current of the detector is due to thermo-emission of the aerosols near the surface of the collector electrode because they absorb the radiant energy of the flame. The work function of the electron for Cs aerosol particles is 1.8 eV (the characteristic minimum of the work function is approximately 1.4 eV). However, in the flame zone rich in oxygen, Cs atoms are oxidized, forming Cs_2O, and in the aerosol zone near the collector electrode the formation of aerosol particles consisting of a mixture of Cs and Cs_2O is possible. These particles have a work function of 0.7–1.0 eV (ref. 12). Taking into account that the amount of the radiant energy of the flame released as radiation can reach 20%[13] and taking into consideration the small work function of the particles (Cs and Cs_2O), one can assume that the main contribution to the background current of the detector is made by the thermo-emission of aerosol particles of Cs and Cs_2O formed.

Hence the TID background current is caused by a thermal ionization mechanism. The appearance of the useful TID signal when organic compounds that contain phosphorus or nitrogen enter the flame can be explained when one takes into account the following facts:

(1) The alkali metal salts are active inhibitors of combustion[14].

(2) Among the products of the combustion of phosphorus- or nitrogen-containing organic compounds in the flame, heavy ions are formed whose mobility

is 1000 times less than that of light ions[15]. These heavy ions combine with Cs ions to form even heavier ions.

(3) When the hydrogen flow-rate is sufficient, a reducing pyrolysis of phosphorus- and nitrogen-containing organic compounds in the flame occurs, resulting in the formation of hydrocarbon radicals[16].

The alkali metal salts present in the flame substantially reduce its temperature. The efficiency of ionization of alkali metal salt vapours (reactions 1–3) and thermo-emission of aerosol particles depend on the flame temperature that is established.

When phosphorus- or nitrogen-containing organic compounds enter the flame in connection with heavy ion formation, the concentration of the alkali metal salt in the flame is reduced and the inhibiting effect of the salt is also reduced (the temperature of the flame increases). The flame temperature increases partly because of the combustion of hydrocarbon radicals formed. The increase in the flame temperature leads to an increase in the efficiency of the ionization of Cs atoms, to an increase in thermo-emission of aerosol particles and hence to the appearance of the useful signal of the detector.

DESCRIPTION OF THE DETECTOR

Examination of different designs of detectors gave results showing that the sensitivity of a TID to an organophosphorus compound varies inversely with its sensitivity to hydrocarbons. This made it possible to draw conclusions about different conditions for the formation of the detector signal from phosphorus-containing organic compounds and from hydrocarbons. In Fig. 1, the relationships between the height of a hydrogen flame and its temperature and between the flame and ion concen-

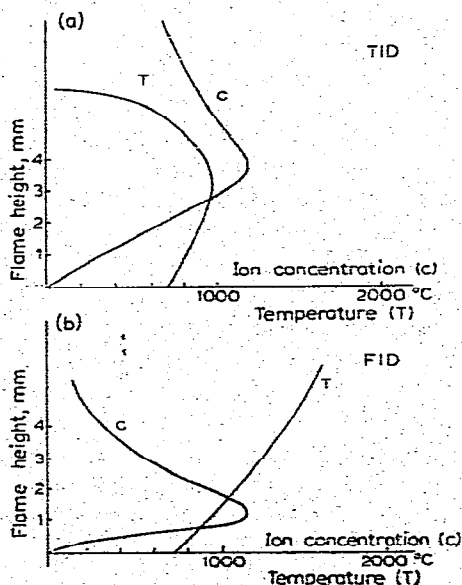Fig. 1. Relationships between the flame height (h) and the temperature (T) and ion concentration (c) for detectors: (a) TID; (b) FID.

tration are shown for the TID (a) and the FID (b)[5,16]. The relationships presented show that:

　　(1) The temperature of the hydrogen flame without an alkali metal salt is substantially higher.

　　(2) The relationships between the height of the flame and the ion concentration and the flame temperature are different for the pure hydrogen flame and the flame with the alkali metal salt, which is indicative of a non-thermal nature of ionization in the FID.

　　(3) The relationships between the height of the flame and the ion concentration and the flame temperature for the TID are similar and the maxima of the curves almost coincide. This is indicative of the thermal nature of ionization in the TID.

　　(4) The zones of the maximum useful signal for hydro　 ʼ ᵒns phosphorus- or nitrogen-containing organic compounds are spatially sepᴀᵣᵥ ᵢ. The maximum ion concentration in the FID at a given gas flow-rate and cross-sᵥ ᵗᵗᵒₙ of the burner nozzle is reached at a distance of about 1 mm from the end of the bᵤᵣₙer. In the TID, the maximum ion concentration under the same conditions is at a hᵢ̇ight of 3–4 mm from the end of the burner.

　　Taking the above conclusions into consideration, it appears possible to design a very promising detector[17]. The drawback of TID designs considered so far is a strong dependence of the background current and sensitivity on the stability of the gas flow-rates applied, which can be explained by the mechanism suggested above, as the changes in gas flow-rates result in changes in the flame temperature.

　　The detector design shown in Fig. 2 was developed allowing for the necessity of separating the zones of the different measuring signals and decreasing the dependence of detector readings upon the gas flow-rates (hydrogen, nitrogen, air). In this detector design, the tip, made of an alkali metal salt, is placed in the collector electrode. The distance between the burner and the collector electrode is about 3 mm. In previously published detector designs[3], the distance between the burner and the collector electrode differs from that chosen here. The potential electrode is made in the shape of a ring covered by a platinum mesh and is located about 1 mm away from the
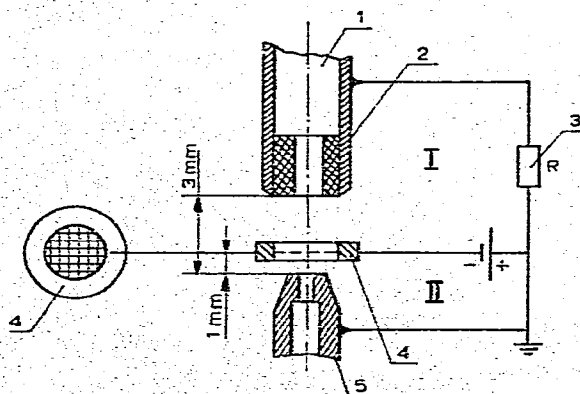

Fig. 2. Schematic diagram of TID. 1, Collector electrode; 2, Cs salt tip; 3, measuring resistance; 4, ring potential electrode with platinum mesh; 5, burner. I, Zone of signal formation from compounds containing phosphorus and nitrogen; II, zone of signal formation from hydrocarbons.

TABLE I

CHARACTERISTICS OF SOME THERMIONIC DETECTORS

Company/type	Optimum gas flow-rates (ml/min)			Potential (V)	Salt	Equilibration time (min)	Linearity	Background current (A)	Sensitivity (g/sec) and test compounds	Reference
	H_2	Air	N_2							
U.S.S.R., Gasochrom 1106T	21	200	28	300	CsBr	20	10^3	10^{-11}	$1 \cdot 10^{-12}$, methylparathion	1
Varian Aerograph, Palo Alto, Calif., U.S.A.	16 ± 0.01	170 ± 0.1	20–40	300	CsBr	10	10^3	10^{-10}	$3 \cdot 10^{-12}$ parathion	2
Pye Unicam, Cambridge, Great Britain	20–40	200–300	30–60	150	CsBr	30	10^3	—	$4 \cdot 10^{-12}$ trimethyl phosphate	7
Perkin-Elmer, Norwalk, Conn., U.S.A.	35–50	450	30	150–300	RbBr	30	10^3	10^{-10}	$2.5 \cdot 10^{-12}$, malathion	8

burner. The size of the mesh and the diameter of the wire influence considerably the selectivity of the detector to different compounds and to the signal-to-noise ratio. The burner is at the potential of the detector case, *i.e.*, at earth potential.

In Fig. 2, it can be seen that in circuit II signals from an organic compound (solvent) can be detected, and in circuit I signals from a phosphorus-(nitrogen)-containing organic compound are detected. The results of the study of the dependence of the sensitivity of this detector on the flow-rates of gases supplied are presented in Figs. 3–5.
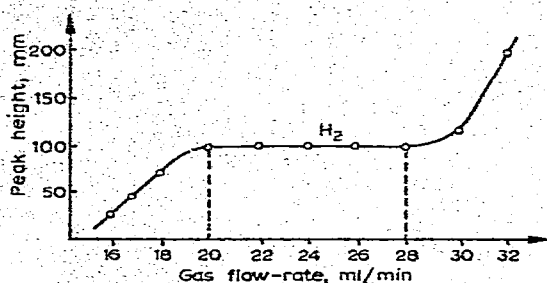
Fig. 3. Relationship between TID sensitivity and hydrogen flow-rate with constant air and nitrogen flow-rates.

It can be seen in Fig. 3 that over a certain range the detector sensitivity is independent of the hydrogen flow-rate; this effect is associated with the insertion of the mesh into the flame zone. The dependence of sensitivity on the flow-rates of air (Fig. 4) and the carrier gas (nitrogen) (Fig. 5) is not appreciable and is such that ordinary systems of stabilizing gas flow-rates allow the detector to be used with maximum sensitivity. The background current of the detector is about 10^{-11} A. The characteristics of the detector are presented in Table I in which, for the sake of comparison, the characteristics of other currently manufactured TIDs are given.

The detector is simple in design and has a minimum limit of detection for methylparathion of $1 \cdot 10^{-13}$ g/sec, which is reliably attained when the detector is used in
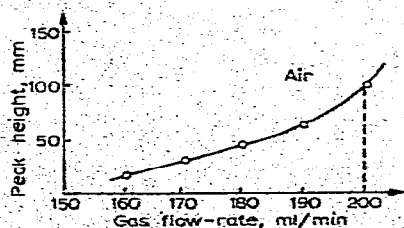
Fig. 4. Relationship between TID sensitivity and air flow-rate with constant hydrogen and nitrogen flow-rates.
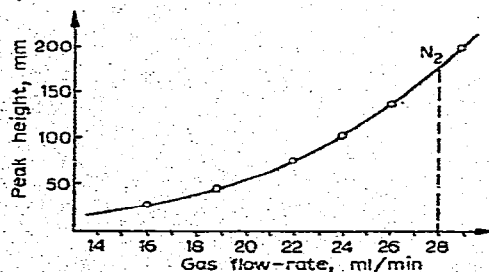
Fig. 5. Relationship between TID sensitivity and the carrier gas (nitrogen) flow-rate with constant air and hydrogen flow-rates.
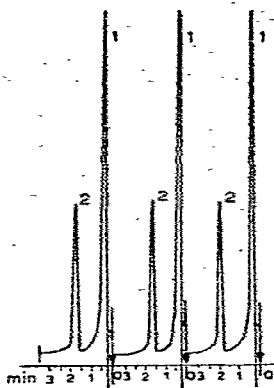
Fig. 6. Chromatogram of a pesticide obtained on a Gasochrom 1106T chromatograph. Peaks: 1, n-hexane; 2, methaphos (methylparathion), $2 \cdot 10^{-6}$ mg/ml. Column temperature, 210°C; detector, 250°C; injector, 200°C. Column length, 1.5 m; I.D., 3 mm; 5% SE-30 on Chromaton (0.2–0.3 mm). Detector voltage, −300 V. Salt, CsBr. Sample size, 1 μl.

conjunction with chromatographic apparatus currently manufactured in the U.S.S.R. At present the detector is mounted on commercial chromatographs and has been approved by the users. In Fig. 6 a chromatogram of pesticides obtained by means of the device is shown.

REFERENCES

1 A. Karmen and L. Giuffrida, *Nature (London)*, 201 (1964) 1204.
2 V. V. Brazhnikov, *Differential Detectors for Gas Chromatography*, (in Russian), Nauka, Moscow, 1974.
3 V. V. Brazhnikov, M. V. Gur'ev and K. I. Sakodynskii, *Chromatogr. Rev.*, 12 (1970) 1.
4 E. Cremer, *J. Gas Chromatogr.*, 5 (1967) 329.
5 V. V. Brazhnikov, M. V. Gur'ev and K. I. Sakodynskii, *Chromatographia*, 3 (1970) 53.
6 M. Scolnick, *J. Chromatogr. Sci.*, 8 (1970) 462.
7 F. P. Speakman and K. Waring, *Column*, 2, No. 3 (1968) 2.
8 B. Kolb, M. Linder and B. Kempken, *Appl. Chromatogr.*, No. 21E (1974)1.
9 M. B. Ojfe, V. M. Poshemansky, V. N. Chernjakin and K. I. Sakodynskii, *Proc. 6th Conf. Gas Chromatogr.*, *Baku, U.S.S.R.*, 1973, p. 38.
10 J. Ševčik, *Chromatographia*, 6, No. 3 (1973) 139.
11 V. B. Eliseev, A. P. Pjatnitsky and D. I. Sergeev, *Thermo-emission Transformers of Energy*, (in Russian), Atomizdat, Moscow, 1970, p. 33.
12 M. A. Margolin and N. P. Rumjantsev, *Fundamentals of Infrared Techniques*, (in Russian), Voenizdat, Moscow, 1957, p. 100.
13 A. I. Roslovsky, V. G. Hasanov and R. H. Gimatdinov, *Fiz. Goreniya Vzryva*, 7 (1971) 577.
14 A. P. Glaskova and V. P. Karpov, *Phys. Combust. Explos.*, 7 (1971) 559.
15 N. I. Shteinboc, *The Application of Radioactive Radiation in Measurement Techniques*, (in Russian), Mashgiz, Moscow, Leningrad, 1960, p. 24.
16 M. Riva, *Rivelatory Ultrasensibili per Gas-Chromatografia*, Carlo Erba, Milan, 1963.
17 E. B. Shmidel, L. I. Kalabina, E. N. Vorona and K. I. Sakodynskii, *Bull. Isobret.* No. 30 (1975) 123.