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COMPARATIVE STUDY OF SOME THERMOIONIC DETECTOR DESIGNS

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SUMMARY

Five thermoionic detectors which have been developed by the authors in the course of studies of the sensitivity mechanism are described. The first design is distinguished by the alkali metal salt tip positioned outside the sensitive volume, whereas the salt vapours are ejected into this volume by an air current. The second design has a newly developed tip at the measuring electrode potential. The third and fourth designs have a lower noise current and dependence on the gas supply flow-rate at the same current signal. The fifth design has wider analytical applications and is standardized with respect to the other variants. Consideration is given to the expected mechanism of the detector sensitivity, based on the thermoionization theory. Experimental data provide support for the correctness of the theory providing allowance is made for the inhibitive and catalytic effects of the alkali metal salt.

INTRODUCTION

The first announcement of the thermoionic technique discovered by Guiffrida dates back to 1964 and the first patent was granted to the same author in 1968². Over the last two decades the interest in this technique has increased and decreased alternately. At the present time the thermoionic detector is widely used in the analytical chromatographs manufactured by leading companies such as Hewlett-Packard, Perkin-Elmer and Tracor (U.S.A.). In the U.S.S.R. this detector is employed in Tsvet-1000 chromatographs.

The importance attached to a selective analysis of micro amounts of phosphorus- and nitrogen-containing organic compounds dictated a permanent improvement in the designs of this detector. The first variants offered practically no analytical applications as their sensitivity was unstable. Initially, efforts were focused on the development of designs and methods of making a tip from alkali metal salts, used in the standard flame ionization detector. The most successful is the one manufactured by Varian (U.S.A.) under high pressure and composed of an alkali metal salt with an appropriate filler. The salt pellet is placed on the upper portion of the detector jet. Similar methods were used to make salt tips for Tsvet-100 chromatographs from 1972 onwards. Unfortunately, the operation of these detectors was unstable and the life of the tips insufficient, these two factors being dependent on the gas and electric supply conditions.

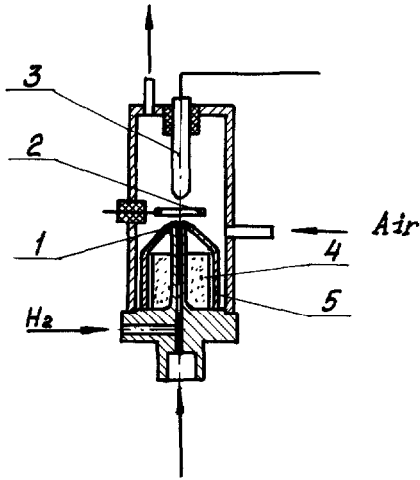


Fig. 1. First design: 1 = jet; 2 = potential electrode; 3 = measuring electrode; 4 = platinum cup with a tip; 5 = quartz cap.

EXPERIMENTAL, RESULTS AND DISCUSSION

We have developed a few seemingly interesting designs of thermoionic detectors.

The first (Fig. 1) comprises a jet (1) made from a quartz capillary, a potential electrode (2) consisting of a platinum ring surrounding the jet, a platinum rod measuring electrode (3) and a tip consisting of a platinum cup (4) filled with a mixture of quartz chips and caesium bromide and mounted on the bottom of the detector. This cup is fitted over the quartz jet (1) and is covered by a quartz cap (5) with a

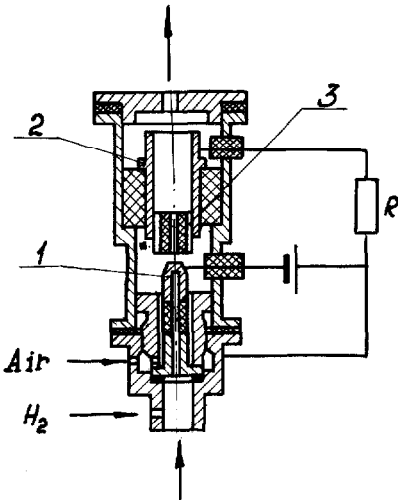


Fig. 2. Detector with a cylindrical quartz tip: 1 = jet (potential electrode); 2 = measuring electrode; 3 = tip. R = entrance resistor of the amplifier.

hole for the jet. The tip is heated and thermostatted by heaters located on the plate carrying the detector. In this detector the tip is positioned inside the ionization chamber but the salt vapours are ejected into the sensitive volume by an air current.

The sensitivity and selectivity of such a detector were found to be relatively low, which, as was revealed later in studies of the sensitivity mechanism, was due to the platinum electrode. It has been reported³ that an alkali metal salt tip has a dual function in that it inhibits the combustion of organic solvents such as hexane and catalyzes that of phosphorus- and nitrogen-containing compounds. At the same time, platinum is known to be a good catalyst for combustion of practically all organic compounds. Therefore the action of platinum largely detracts from the effect of the alkali metal salt.

The second detector (Fig. 2) is characterized by the construction and arrangement of the tip^{4,5} which as comprises a quartz cylinder whose inner surface bears an alkali metal salt and is placed inside the cylindrical measuring electrode (2). For the first time in thermoionic detectors the tip was at the potential of the measuring electrode. This design is very much like that of the flame ionization detector with some features characteristic of thermoionic detectors.

The selectivity of this detector was believed to be insufficient. Analysis of experimental data showed that signals from the organic solvent and phosphorus-containing organic compounds were generated at various flame heights. At a nozzle diameter of 0.5 mm and flow-rates of 20, 200 and 25 ml/min (for hydrogen, air and nitrogen, respectively), the organic solvent signal was generated at a distance of 1 mm from the jet exit section and that of the phosphorus-containing compound at 3 mm from the same section. This permitted the design to be improved in such a way that the organic solvent ions were detected by the measuring electrode 3.

For this purpose (Fig. 3) an additional annular electrode (2) was placed be-

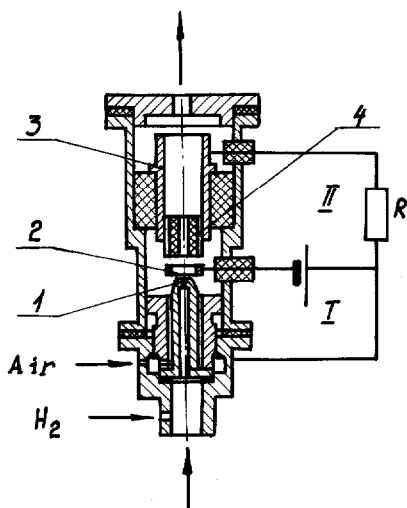


Fig. 3. Detector with an additional ring: I = zone of formation of the signal from the phosphorus- and nitrogen-containing organic compounds; II = zone of formation of the signal from the organic solvent. 1 = Jet; 2 = ring (potential electrode); 3 = measuring electrode; 4 = tip.

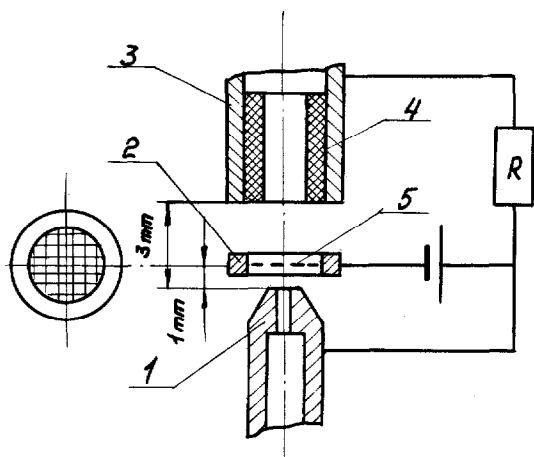


Fig. 4. Relative arrangement of the tip, ring and jet: 1 = jet; 2 = ring (potential electrode) with a grid; 3 = measuring electrode; 4 = tip; 5 = platinum grid.

tween the jet (1) and the measuring electrode 3, at a height of 1 mm from the jet exit section, and played the rôle of a potential electrode⁶. Ions generated in the zone between the jet (1) and electrode 2 were collected in zone I, and those generated between the tip (4) and the same electrode were collected in zone II. The addition of electrode 2 made it possible to improve the performance of the system in that the dependences of the noise current and the useful signal on the supply gas flow-rates were decreased without affecting the latter's magnitude.

Further improvements in performance required clarification of the sensitivity mechanism. Special studies demonstrated that the ionization processes in the sensitive

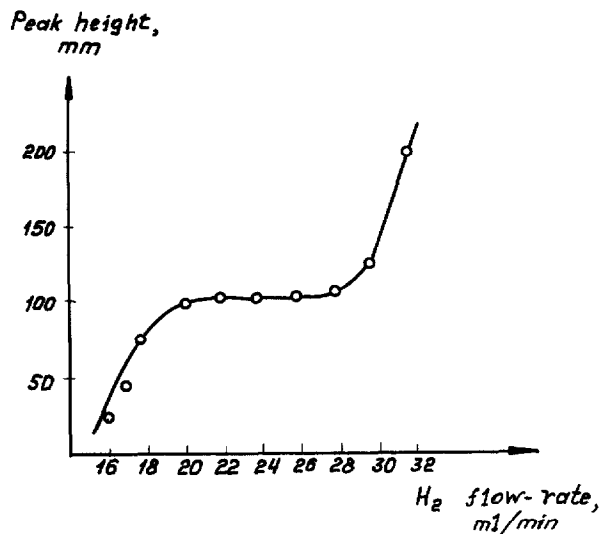


Fig. 5. Dependence of the sensitivity (peak height) on the hydrogen flow-rate.

volume were of a thermal nature, being governed by the thermal emission of electrons from the surface of the alkali metal salt aerosols. This explained the dependence of the detector performance on the stability of the supply gas flow-rate, with the implication that flow-rate changes resulted in a corresponding change in the temperature field in the sensitive volume. Thus a new design (Fig. 4) was developed in which the annular potential electrode (2) was covered with a platinum grid (5)⁷.

With such a detector, a fairly large variation of the hydrogen flow-rate (between 19 and 32 ml/min) did not affect the output signal (Fig. 5), whereas the temperature field in the sensitive volume varied only slightly. The detector performance was very stable and the lifetime of its alkali metal salt tip exceeded 1000 h.

This detector, as part of a Gazokhrom 1106T chromatograph, was applied commercially. The design was also used in experiments to provide support for the expected sensitivity mechanism of the thermionic detector, based on the assumptions that the alkali metal salts inhibit the burning of organic compounds free from phosphorus, nitrogen and halogens and, at the same time, catalyze the burning of phosphorus-containing compounds. It follows that ionization in this detector is of a thermal nature. In other words, the burning of the phosphorus-containing compounds increases the flame temperature, which, in turn, enhances the number of ionized molecules of the alkali metal salt.

The experiments consisted essentially in temperature measurements in the tip zone and at various heights of the potential electrode during the addition of a metaphos sample dissolved in hexane. The addition of 1 μ l of pure hexane increased the temperature by 1.1°C and 1 μ l of metaphos in hexane (10^{-3} mg/ml) increased the temperature by 2.2°C. This permitted the conclusion that the ratio of the increases in flame temperature when burning equal amounts of phosphorus-containing organic compounds and organic compounds without phosphorus was 10^6 , which corresponds to the detector selectivity.

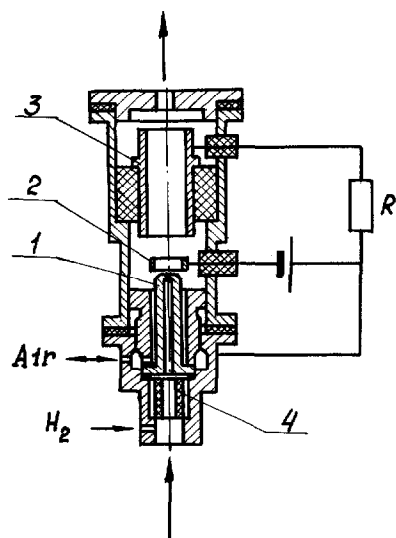


Fig. 6. Detector a tip moved out of the flame zone: 1 = jet; 2 = potential electrode; 3 = measuring electrode; 4 = tip.

Simultaneously with these measurements the ionization detector current was recorded. A comparison of the readings indicated that the peak values on the chromatogram were proportional to the temperatures. A temperature at a ring zone was measured under the same conditions. The results obtained showed that the temperature in the ring zone decreased upon addition of the phosphorus-containing organic compounds. This experiment demonstrates the validity of the thermoionization theory taking into account the inhibitive and catalytic effects of the salt.

To extend the analytical applications of the thermoionic detector and to standardize it with respect to other detectors widely used in gas chromatography, a design was created in which the alkali metal salt tip (4) was moved out of the sensitive volume (Fig. 6)⁸. Although some similar designs exist^{9,10}, that shown in Fig. 6 is radically different in that it contains alkali metal salt vapours passing through all the flame zones where the signals of the solvent and phosphorus- or nitrogen-containing organic compounds are generated. Therefore high sensitivity and selectivity at detector temperatures up to 3000°C become practical. An additional benefit is a simple detector construction.

To summarize, the most suitable design is, in our opinion, that presented in Fig. 4, *i.e.*, a Gazokhrom 1106T type. It minimizes the dependence of the readings on the stability of the gas supply flow-rate and ensures the interaction of the compound analyzed both in the vapour phase (by heating the tip to high temperatures with the flame) and on the tip surface. The useful signal is most likely to be due both to the interaction with this phase and with the tip surface. Thus, for the time being, this design can be regarded as the most favourable for practical uses.

CONCLUSIONS

(1) The detector design used in the Gazokhrom 1106T chromatograph, distinguished by a high performance stability and extended lifetime of the alkali metal salt tip (over 1000 h), is recommended.

(2) A comparative study of designs of thermoionic detectors revealed that the most suitable is that where the compound to be analyzed interacts both in the vapour phase and on the tip surface.

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