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A GAS CHROMATOGRAPHIC ARGON TRIODE-TYPE DETECTOR WITH A NICKEL-63 SOURCE

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SUMMARY

The construction and characteristics of an argon triode-type detector designed for gas chromatography in which nickel-63 is used as the ionization radiation source are described. The detector can operate at temperatures up to 400°. Measurements showing the influence of the dimensions of the electrodes on the characteristics of the detector are presented. Using these results, a detector was developed in which the third electrode current depends minimally on the temperature, carrier and secondary gas flow-rates and voltage. The base current of the third electrode was about 100 times lower than the argon detector base current. The detectivity of the detector is 10^{-12} g/cm³ for benzene and *n*-pentane in argon.

Investigations of the electric field distribution inside the detector are described and conclusions concerning the possibility of building an argon triode-type detector with different triode and anode shapes are drawn.

INTRODUCTION

In 1958 Lovelock¹ described the construction and general physical principles of the operation of a radioactive argon detector for gas chromatographic analysis. Since then, however, many of phenomena responsible for the detection have remained unexplained and much can be done to improve the constructional parameters of the detectors.

This paper describes an argon triode-type detector for gas chromatography and is a continuation of our previous work²⁻⁴ on the elucidation of the phenomena and the improvement of the detector parameters. The physical principles of the operation of the detector and the mathematical expressions for the magnitude of the signal due to a given gas sample have been considered by Lovelock^{1,5,6}, Collinson *et al.*⁷, Knapp⁸, Leonhard and Bothe⁹, Dressler *et al.*¹⁰, Lasa¹¹ and Lasa and Jeleń¹².

PRINCIPLE OF OPERATION

The argon triode-type detector consists of two cylindrical electrodes placed in the argon carrier gas flowing from the chromatographic column. One of the electrodes is covered with a radioactive source (nickel-63) emitting beta-particles with a maximum energy of about 67 keV, the decay half-life being 123 years.

The electrodes are supplied with high voltage of about 1000 V and ion-electron pairs formed by the beta-particles are collected. Apart from ionization, beta-particles, in collisions, excite argon atoms to the resonance and metastable states. The latter play a fundamental role in the operation of the detector. The metastable Ar^m species collide with molecules M , which are eluted from the chromatographic column and are ionized by the Penning effect:



The resulting increase in the electrical current flowing through the detector is to some extent proportional to the amount of substance eluted. The relationship between the increase in current and the vapour concentration and the basic reactions was derived by Lovelock^{5,6}, Collinson *et al.*⁷ and Knapp⁸.

It is evident that the Penning process can occur with some efficiency only if the ionization potential of the vapour molecule is equal to or less than the stored energy of the metastable atoms (11.7 eV). This condition is satisfied by nearly all organic compounds, which are therefore analyzed mainly with an argon-type detector. From this point of view, the argon-type detector is equivalent to the flame ionization detector, but has some advantages as there is no need to use hydrogen and its sensitivity and detectability are greater if the detector is properly constructed. The use of nickel-63 as the ionization source permits the detector to operate at temperatures up to 400° without the risk of detachment of the source and the consequent radioactivity hazard.

GEOMETRY OF THE ACTIVE SPACE OF THE DETECTOR

The argon triode-type detector is illustrated in Fig. 1. The detector consists of the radioactive source (1) (nickel-63) and the anode (2) through which the carrier gas and analyzed gases and vapours are introduced. Scavenge gas introduced through the inlet (5) ensures that components flow in the near neighbourhood of the anode (2) before leaving through the outlet (6). A high negative voltage supplied to the radioactive source results in the collection of ions and electrons produced by ionization and accelerates electrons towards the anode to such an energy that it is possible to excite the argon atoms to the metastable state in inelastic collisions.

There is a third electrode between the radioactive source (cathode) and the anode. The triode is situated in such a way that the ionizing current flowing to it is minimal when only carrier gas passes through and the detector operates in the field-intensified current region. If any other vapour or gas molecules eluted from the column are present in the carrier gas then, after their ionization, positive ions have a shorter path to the triode than to the cathode and the resulting increase in current is considerable.

In this type of detector, the third electrode is connected to an electrometer. The correct positioning of the triode relative to the anode is difficult when one wants to obtain the maximum possible sensitivity, detectability and dynamic range on the one hand and the minimum dependence of basic current upon the temperature, gas flow and the voltage supplied to the electrodes on the other. To find this optimal position of the electrodes, investigations have been carried out⁴ and the present work is a continuation of these investigations.

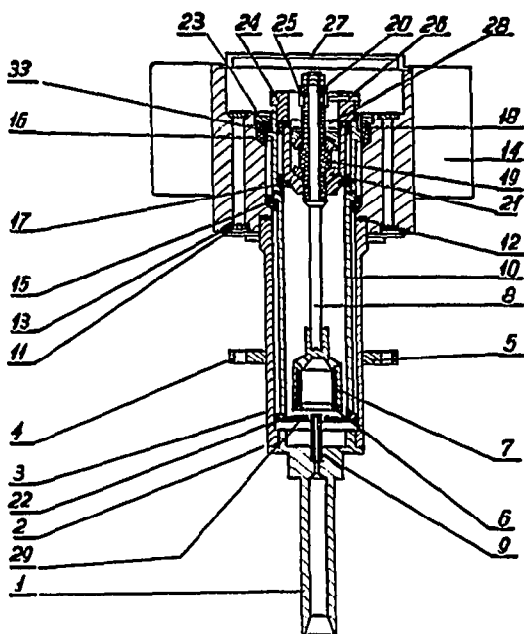
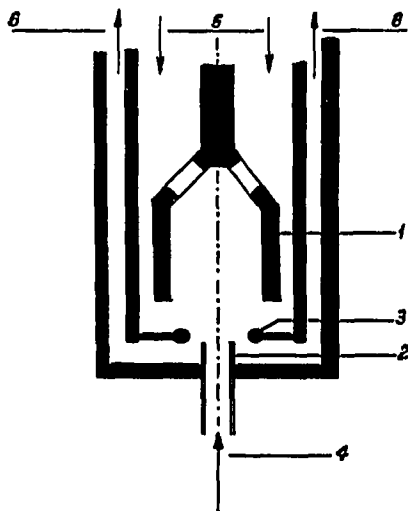


Fig. 1. Diagram of the active space of the argon triode-type detector. 1 = Cathode with nickel-63 on the inner side; 2 = anode; 3 = triode; 4 = carrier gas inlet; 5 = secondary gas inlet; 6 = gas outlet.

Fig. 2. Cross-section of the argon triode-type detector. Numbers are explained in the text.

CONSTRUCTION OF THE DETECTOR

A cross-sectional view of the detector is shown in Fig. 2. The detector consists of the head (14), to which the casing (3) terminating in a tail-piece (1) is screwed. The centrally placed electrode (8) ends in the handle (7) of the radioactive source secured in it by means of a nut (6). The electrode (8) is fixed by means of an insulator (19), cones (21) and a nut (33) in the shield (11). This shield is fastened in the electrode (10) by means of insulators (17, 18) and a nut (24). There are three screws in the nut (24), which permit the regulation of the central position of the electrode (8). The electrode (10) is fixed in its upper part in the head (14) by means of insulators (15, 16) and a nut (23). The lower part of the electrode (10) ends in a nut (22) securing the ring (23), which is the third electrode of the detector. The detector is fastened in its own thermostat with a separately regulated temperature by means of a supporting collar (5).

The carrier gas enters the detector through the end of the tail-piece (1) and the anode fixed in it. The secondary gas is introduced through the inlet place in the side wall of the detector head. In the side walls of the head (14) there are also the outlet of both gases, terminals of the electrodes (8, 10) and the inlet and outlet of the cooling water running in the channels of the head (14).

An important feature of the construction is that there are no insulators in the active space of the detector but all of them are placed in the head (14) and cooled in such way that it is possible to keep their temperature constant compared with that of the thermostat, inside which the active space of the detector is situated. The efficacy of

an identical cooling system was shown earlier by Lasa *et al.*³. The maximum allowable operating temperature of the detector equipped with nickel-63 as a source is 400°.

EXPERIMENTAL

In order to determine all of the necessary parameters of the above detector, the following characteristics were measured: 1, the dependence of the ionizing current of the detector on temperature, $I=f(T)$; 2, the dependence of the ionizing current on voltage, $I=f(U)$; 3, the influence of the carrier and purge gas flow-rates on the ionizing current; and 4, the increase in the ionizing current of the detector due to the concentration of the analyzed compound in the sample, $\Delta I=f(C)$. In measurement of a particular characteristic, only one parameter was changed, all the others being kept constant.

The first three dependences were measured with the detector connected to an injector port system with an empty 3-m chromatographic column. In the fourth case, a 3-m column packed with 10% squalane on Chromosorb W was used. The $\Delta I=f(C)$ characteristics were found for *n*-pentane and benzene using the exponential dilution flask method described by Lovelock⁵ and the measuring system of Lasa and Broś⁴. The detector was placed in the head of an N-503 chromatograph (Mera, Wrocław, Poland), provided with flow and temperature regulators. A ZWN-2.5 high-voltage supply (Polon, Warsaw, Poland) was used and the ionizing current of the third electrode was measured with a VA-7-51 electrometer (Vakutronik, Dresden, G.D.R.).

An electrolytic trough¹³ filled with tap water, which obeys Ohm's law, was used to find the field distribution in the detector. The potential gradients were obtained by applying a voltage of about 10 V to a scale two-dimensional model (Fig. 1) (an enlargement of five times was chosen) immersed in the electrolyte. The electrolyte trough was not tilted from the horizontal as in the work of Collinson *et al.*⁷ because it was not intended to simulate the exact logarithmic variation of potential with the distance from anode to cathode.

RESULTS AND DISCUSSION

The detector characteristics were found for three anodes of different lengths, designated 1, 2 and 3 from the longest to the shortest. The dependence of the ionizing current on the voltage supplied for six different temperatures from 50° to 350° are presented in Fig. 3. The length of the anode and its position relative to the triode are of particular importance and as the anode becomes shorter the dependence of the basic current on voltage becomes less. An interesting phenomenon was observed for anode 2, *viz.*, an initial slight fall in the stationary current when the voltage was increased from 300 V to about 1000 V. This was unexpected and is unexplained. The influence of temperature on the ionizing current, illustrated in Fig. 4 is also related to the dimensions of the anode.

When examining the results, it might be concluded that anode 3 is the best, because it shows the least dependence of the stationary current on the temperature and voltage. This is not so, however, because for this anode breakdown can occur very easily and the points shown in Fig. 3c for the measurements at the highest volt-

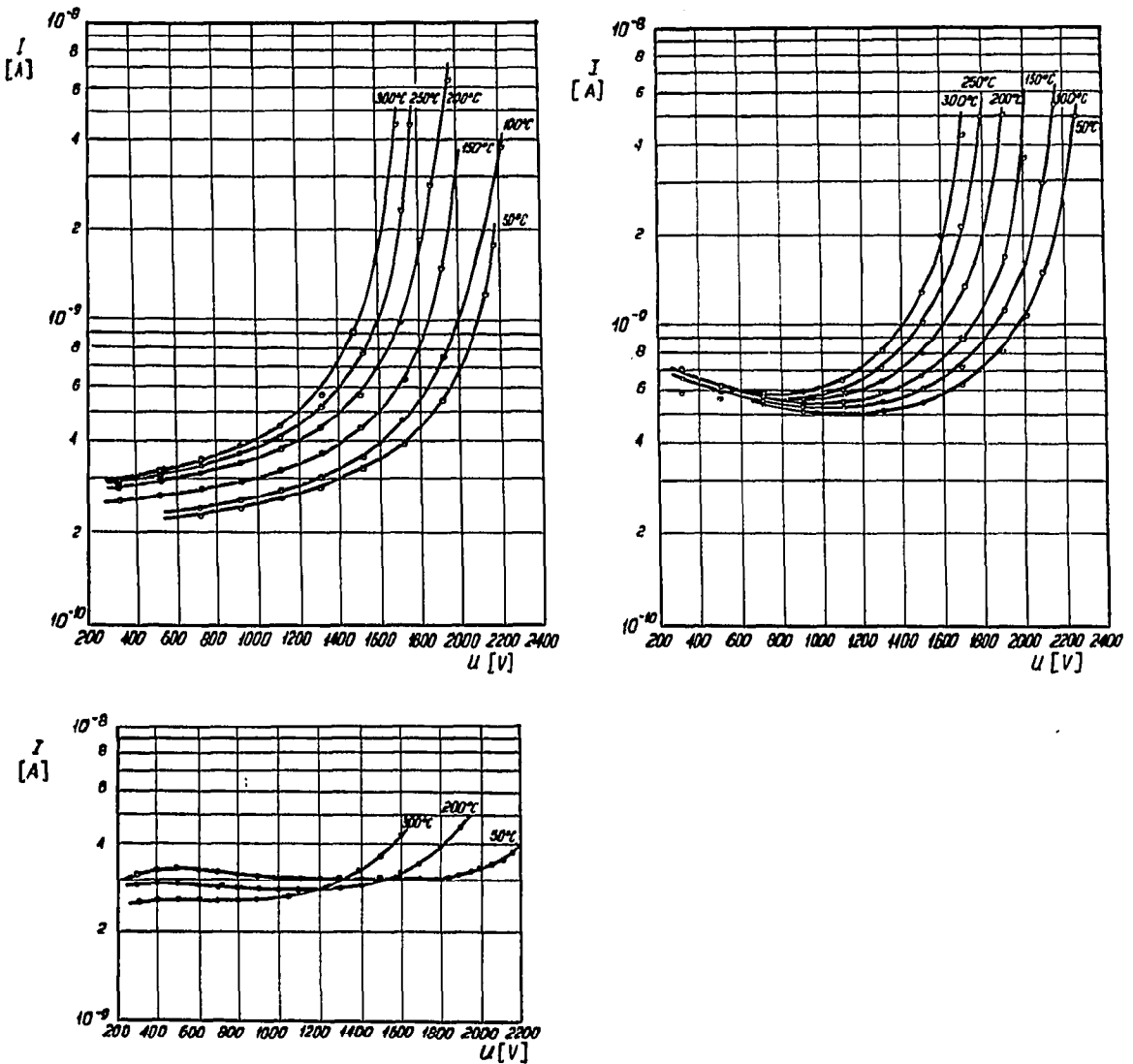


Fig. 3. Current-voltage characteristics of the argon triode-type detector at different voltage supplies. Carrier and secondary gas, argon; flow-rate = 50 cm³/min for both. (a) Anode 1 (the longest); (b) anode 2; (c) anode 3 (the shortest).

ages are those at which breakdown is observed. For anode 3, the shortest one, the detector would have a very good sensitivity but very little dynamic range.

Anode 2 proved to be the best. For this anode, especially at low temperatures, the influence of the voltage supplied on the magnitude of the basic current is small in the range of voltages used, *i.e.*, from 800 to 1400 V. For the voltage of 1100 V, a change in temperature from 50° to 300° causes an increase in current of only 10%. It is very difficult to achieve this advantage in radioionization detectors. The ionization

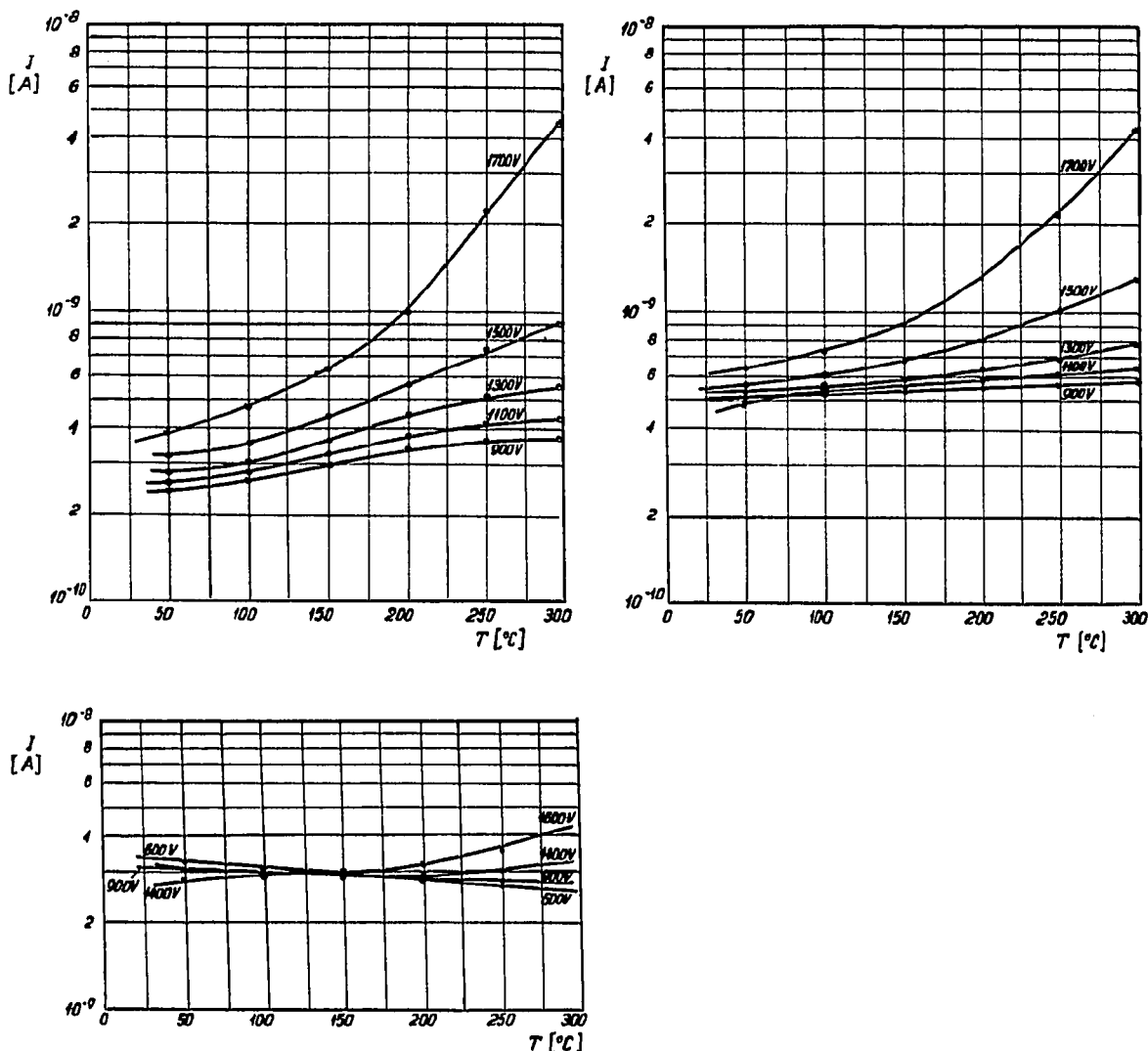


Fig. 4. Dependence of the current of the argon triode-type detector on its temperature. Carrier and secondary gas, argon; flow-rate = $50 \text{ cm}^3/\text{min}$ for both. (a) Anode 1; (b) anode 2; (c) anode 3.

current of the detector is about 100 times less than in the classical argon detector and has a plateau of about $6 \cdot 10^{-10} \text{ A}$.

The influence of the carrier and scavenge gas flow-rates on the detector current is also small (Fig. 5).

The relationship between the detector signal and the concentration of benzene are shown in Fig. 6 for anodes 1 and 2. These curves were the basis of the determination of the sensitivity and the dynamic range given in Table I together with other parameters.

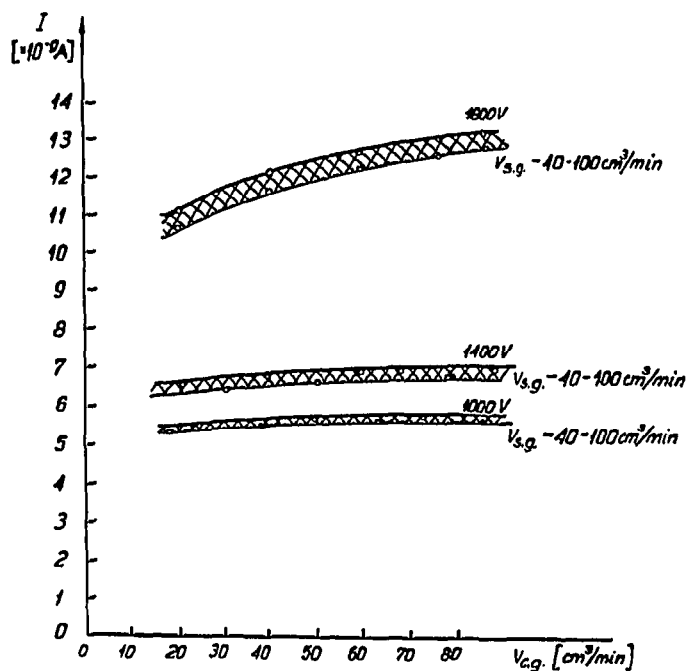


Fig. 5. Dependence of the current of the argon triode-type detector on the carrier and secondary gas (argon) flow-rate for anode 2.

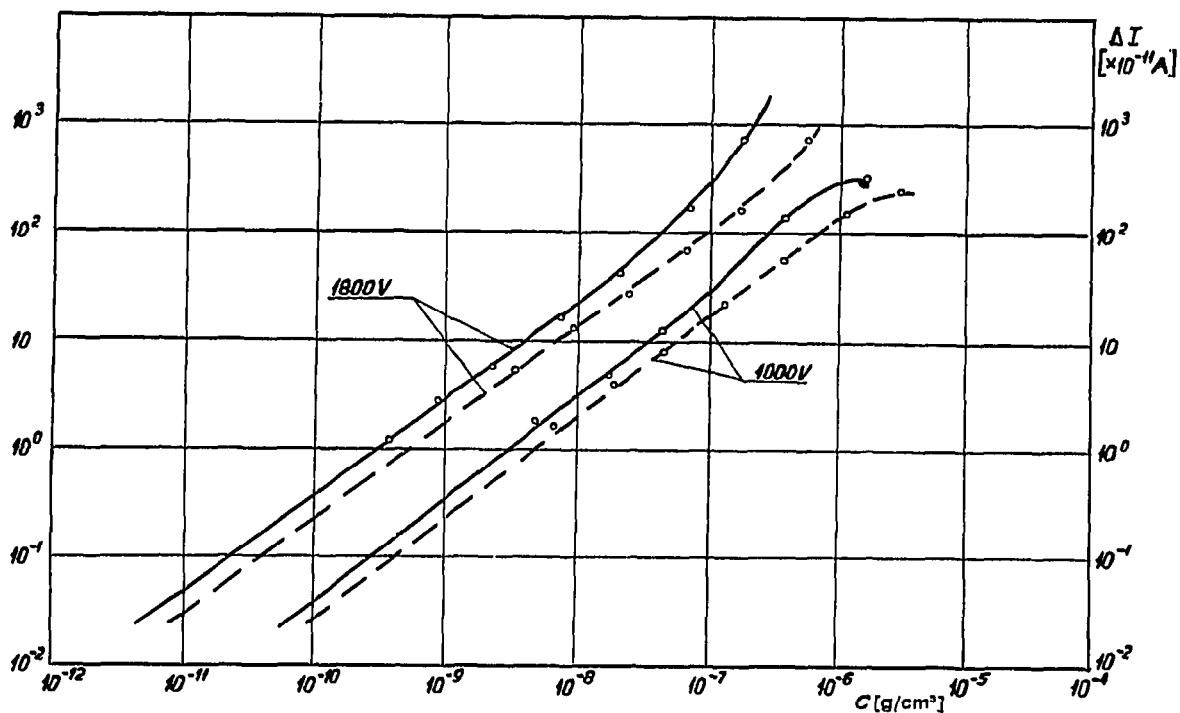


Fig. 6. Response curve for benzene. ----, Anode 1; —, anode 2.

TABLE I
BASIC PARAMETERS OF THE ARGON TRIODE-TYPE DETECTOR

Parameter	Value
Sensitivity	0.02 Ci/g
Detectability (for <i>n</i> -pentane)	10^{-12} g/cm ³
Basic current for a voltage supply of 1000 V	$5 \cdot 10^{-10}$ A
Noise level for low voltage	10^{-12} A
Dynamic range	$5 \cdot 10^4$
Maximum operating temperature	400°
Voltage supply range	700–1600 V
Carrier gas	Argon
Secondary gas	Argon
Radioactive source	Nickel-63, 10 mCi

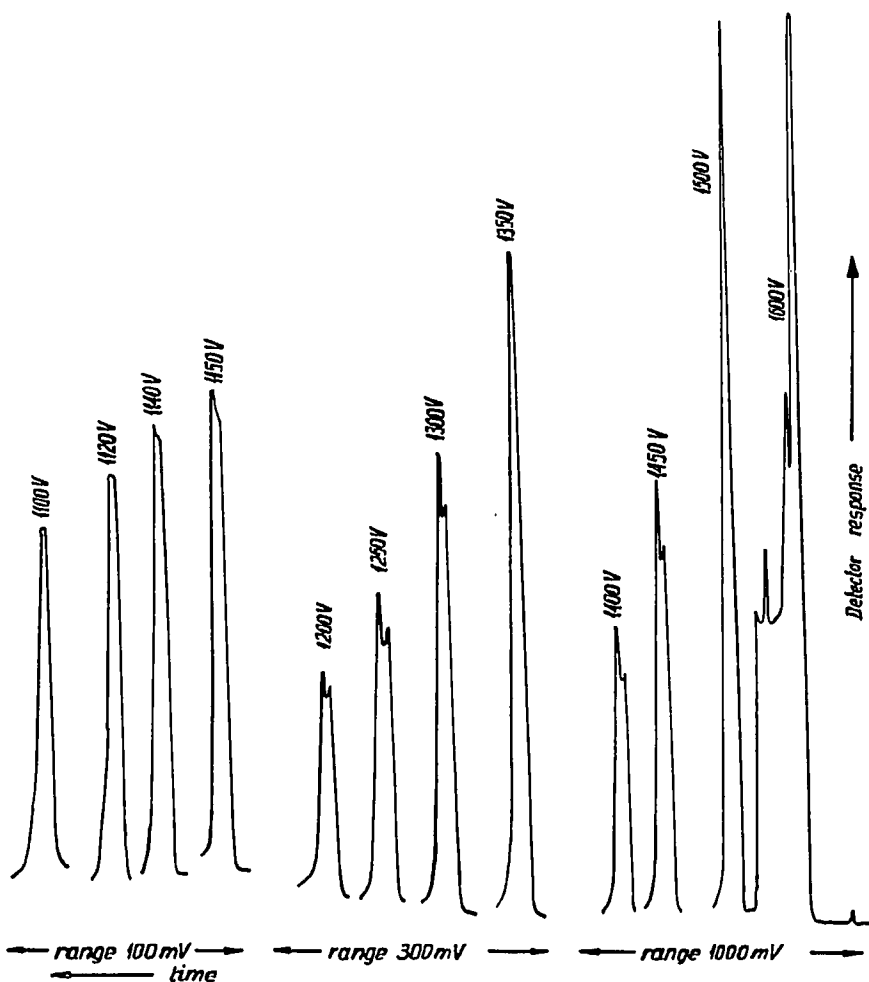


Fig. 7. Effect of applied voltage on the peak shape for 0.25 μ l of benzene.

The phenomenon of saturation connected with the high concentration of the compound being analysed was observed only for low voltages. For higher voltages and for concentrations above about 10^{-7} to 10^{-6} g/cm³ benzene, breakdown occurs. These effects can be seen better in Fig. 7, which shows the influence of the applied voltage on the peak shape for 0.25 μ l of benzene. It can be seen that only a decrease in the voltage to 1120 V cancels out the deformation of the peak top. For higher voltages, one may see the peak deformation first and the peak division described by Lasa¹¹, and Lasa and Jelen¹², and for voltages above 1400 V the detector does not function correctly with the amount of sample used.

The possibility of easy electrical breakdown is a disadvantage and can lead to the destruction of the high-voltage supply and the measurement system or even the detector itself. For this reason, the voltage supply and the electrometer should be protected from overloading in the current region of 10^{-6} A. Following the suggestion originally made by Lovelock⁵, an attempt was made to eliminate the electrical breakdown by connecting a resistor of about 1 M Ω –1 G Ω between the detector and the high-voltage supply. It failed to produce the expected results but, on the other hand, a considerable decrease in the dynamic range was observed. Attempts to bias the triode with a slight negative or positive potential were also unsuccessful.

In order to understand better the reasons or such a considerable dependence of the operating parameters on the length of the inlet anode, investigations of the equipotential line distribution in the active space of the detector were made for the two-dimensional model (Fig. 1). Because the shape of the triode is as shown in Fig. 8, two measurements for each anode were carried out, *viz.*, for the cross-section A along the connecting arms and for the cross-section B along the niches. Fig. 9 shows examples of the field distribution for anode 2.

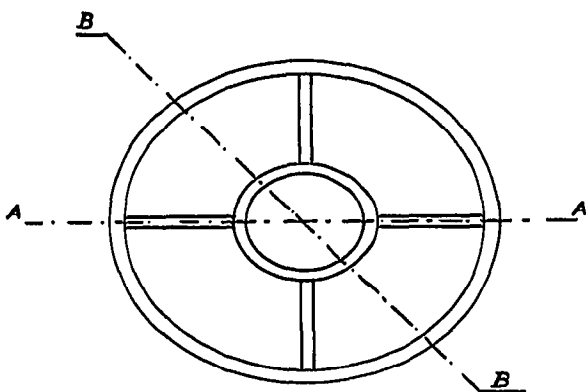


Fig. 8. Shape of the electrode of the detector.

CONCLUSIONS

The argon triode-type detector described can be used for trace analysis if it is supplied with a sufficiently high voltage and the determination of higher concentrations can be made with a correspondingly lower voltage.

The detector has the valuable feature that the basic current is independent of temperature, the applied voltage and the carrier and purge gas flow-rates. For these

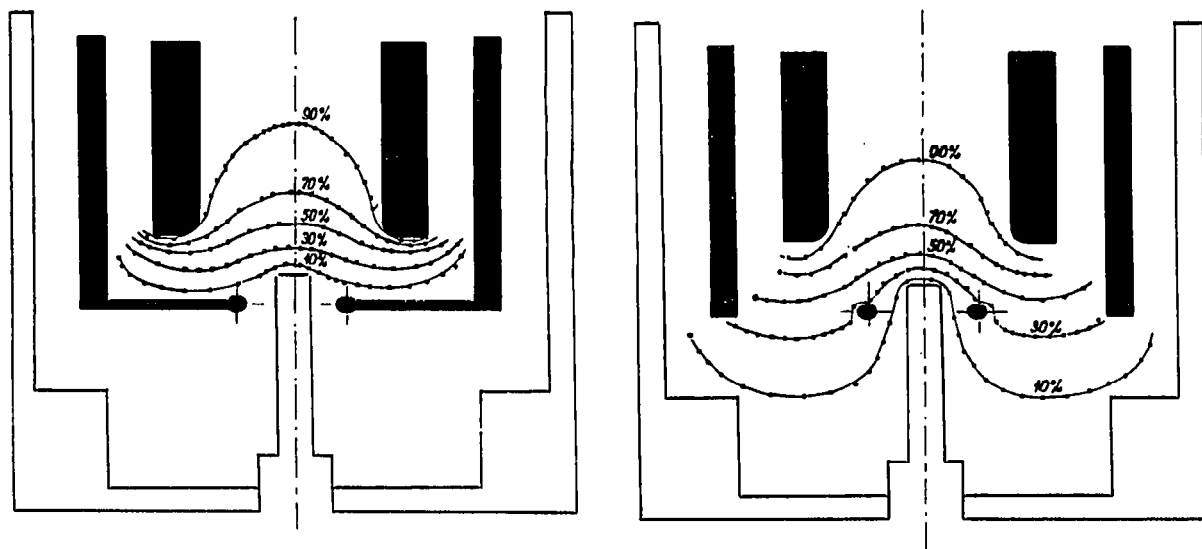


Fig. 9. Distribution of the equipotential lines of the electric field inside the argon triode-type detector for anode 2. (a) For cross-section A (Fig. 8); (b) for cross-section B of the triode.

reasons, it can be operated with temperature programming. By increasing the voltage, it is possible to decrease the minimal detectable amount of the substance being analyzed without any considerable change in the zero line of the detector. In connection with the strong influence of the mutual position of the electrodes on the detector characteristics, it seems worth-while to try to construct the triode in the shape of the equipotential line for the cross-section B (Fig. 9b) and the inlet anode closed at the end and open on the side wall, so that the carrier gas may flow directly into the region of the highest field. Appropriate work is in progress.

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