Some Characteristics of a β-Ray Argon Tetrode Detector

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Lovelock [1] has suggested that the insertion of a fourth electrode into the argon triode gas chromatographic detector could decrease the noise level and thus increase its sensitivity. Because the author is not aware of any detailed description of the argon tetrode in the literature, some of its properties are reported below.

Experimental. The detector cell is shown in Fig. 1. The collector electrode is connected to the electrometer grid, with a resistance of 95 M Ω to earth. The screen grid voltage is taken from a separate battery. If not otherwise specified, the screen grid has a series resistance of 10 M Ω, and the anode 1 M Ω. 10 mC ^{90}Sr is used as the source of electrons. The high frequency cut-off of the measuring system is at about 50 cps.

The cell was calibrated by the exponential dilution method [1,2]. During most measurements the calibration vessel and the detector were kept at 100°C, and the gas velocity at 100 ml/min. Butane was used as the test substance. The argon gas was purified by means of a trap containing Linde's molecular sieve, 4 Å, kept at −76°C. The detector response was calculated according to formula (1).

$$\ln C = \ln C_0 - \frac{U \cdot t}{V} \qquad (1)$$

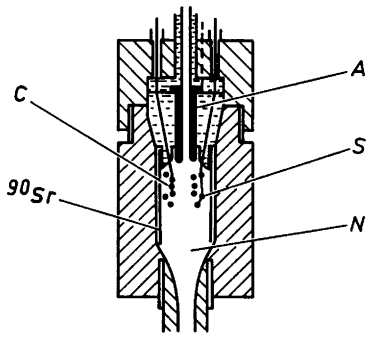

Fig. 1. Lined parts = brass; dotted parts = PTFE; A = anode; S = screen grid; C = collector grid.

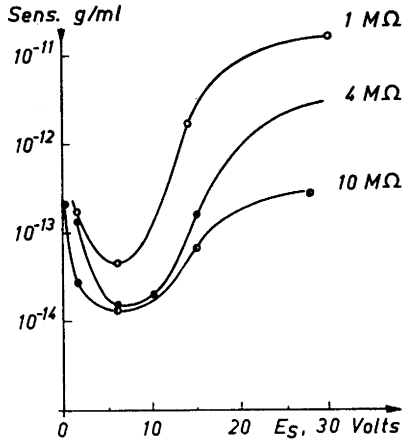

Fig. 2. Dependence of sensitivity on screen grid voltage with the screen grid series resistance as parameter.

(C_0 = initial concentration of butane, C = concentration at time t, U = gas velocity, V = volume of the calibration vessel).

Because the cell was designed for use with packed columns, no scavenge gas is used. The inside of the cell is pear-shaped to give a smoth flow of carrier gas. A diffusion net of wire gauze [1] inserted at N (Fig. 1) had no influence on the signal/noise level.

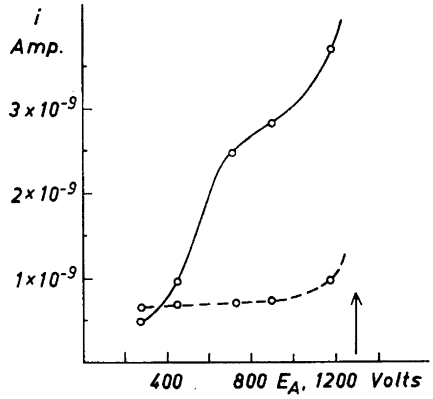

Fig. 3. Anode (— O —) and collector grid (- - - O - - -) currents as a function of anode voltage. Arrow indicates breakdown. Screen + 10 V.

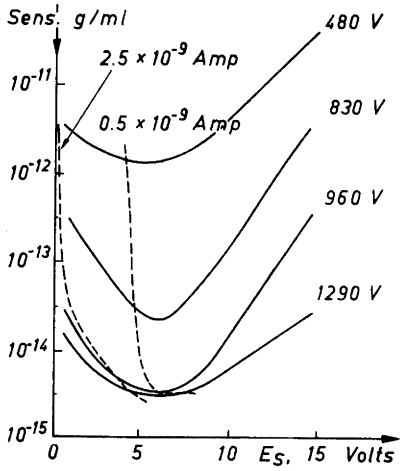

Fig. 4. Ordinate: Concentration of butane giving a signal = 2 × noise. Abscissa: Screen electrode voltage. Solid lines: Sensitivity at different anode voltages. Broken lines connect points with same collector current when pure argon flows through the cell.

The collector grid current with pure argon in the cell, as well as the sensitivity, remained unchanged when the gas velocity was increased from 70 cm³/min to 150 cm³/min.

As shown in Fig. 2, the value of the screen grid series resistance must be at least four times the anode series resistance, or the electron density at the anode will be seriously lowered. Also, the screen current should be kept to a minimum to keep the noise low.

From the plot of the anode voltage, the anode current and the collector current at a constant screen voltage (Fig. 3), it is seen that a measurable collector current exists at low anode voltages. This might be due to a secondary emission of electrons from the collector electrode due to the radiation. The collector current might partly be caused by the reaction[3]

$$A^* + A^* \rightarrow A + A^+ + e^-$$

at the higher anode voltages. The collector current remains fairly constant until the screen grid loses control over the discharge. Then the noise, which during the flat part of the collector current curve is $< 10^{-13}$ A, rises sharply.

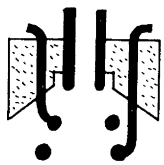

Fig. 5. Second electrode configuration.

At room temperature, the collector current and the noise with pure argon is not markedly dependent on the screen grid voltage within the range + 4 — + 10 V. From the relationships shown in Fig. 4, it is concluded that the positive screen causes an increase in the collecting efficiency of positive ions or a change in the space charge within the cell. Also, the screen prevents the collection of positive argon ions formed near the radiation source.

The ionization efficiency of the cell at maximum sensitivity is about 20 Coul/gr. The linear range is about 10^3.

To keep the detector stable at temperatures above 190°C, the collector electrode should be provided with an earthed guard ring, and precautions against creeping of the PTFE insulation should be taken.

In high sensitivity work it must be observed that the maximum allowed working temperatures for stationary phases will be about 80°C less than the values recorded in the literature.

It may be mentioned that if the electrode configuration in Fig. 5 is used, the maximum sensitivity for organic substances is about ten times lower. However, with this construction the screen electrode may be used for collection of negative ions, formed by electron capture. In this way a sensitivity of about 5×10^{-8} g/ml for oxygen and carbon dioxide has been observed.

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