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ARGON IONIZATION DETECTOR SENSITIVE TO HYDROGEN CONSTRUCTION AND MECHANISM OF OPERATION

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SUMMARY

The construction and optimal operating parameters of a radioionization detector having a sensitivity towards hydrogen as high as 10^{-11} g/sec are presented. The device also detects carbon monoxide, methane and ethane. Technical-grade argon is used as a carrier gas.

The mechanism of operation involves the occurrence of either a Hornbeck-Molnar type-reaction ($\text{Ar}^* + \text{H} \rightarrow \text{ArH}^+ + \text{e}^-$) or a Penning ionization of the products of the decomposition of carbon monoxide, methane and ethane.

INTRODUCTION

In a recent paper¹ we described a new version of a radioionization detector, using technical-grade argon as a carrier gas, which is sensitive towards hydrogen, carbon monoxide, methane and ethane.

In this paper the details of the design and operating conditions that affect the operation of the detector are given, and a hypothetical mode of operation is proposed.

EXPERIMENTAL

Three detectors of varying design (Fig. 1) were investigated. The essential feature of all three detectors is a titanium-tritium foil with an activity of 2-2.5 Ci (obtained from the Institute of Nuclear Research, Warsaw, Poland).

In design I, a simple cylindrical cell (see Fig. 1a) employs flat parallel-plate electrodes (28 mm in diameter) so as to produce a uniform field. The distance between the electrodes could be varied over the range 1-6 mm, thereby changing the volume of the detector from 0.6 to 3.7 cm³. The lower electrode was provided with the tritium source.

In design II, the tritium source deposited on a cylindrically shaped strip (30 × 10 mm) is inserted into a simple cylindrical ion chamber (I.D. 10 mm, volume 1.5 cm³), much similar to that described by Lovelock². The collecting electrode can be readily exchanged.

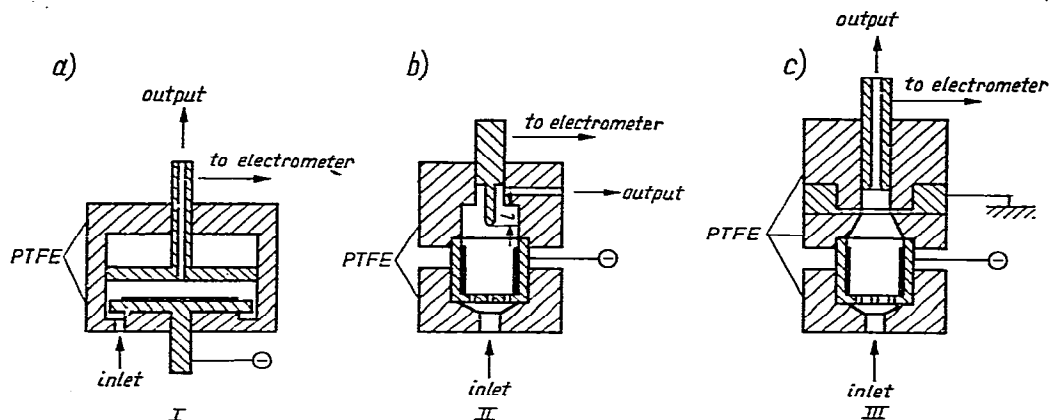


Fig. 1. Three versions of the investigated detectors (schematic).

In design III, a triode, shown in Fig. 1c, consists of a cylindrically shaped cathode (I.D. 10 mm, height 12 mm) with the tritium source placed inside (10 × 30 mm strip).

The second grid electrode, in the form of a ring coaxial with the other two, 6 mm in diameter, is placed at a distance of 8 mm from the cathode. The column effluent leaks into the apparatus through a fine orifice (1.5 mm in diameter) drilled in the centre of a cylindrical anode (5 mm in diameter). The distance between the grid and the anode can be varied over the range 0–8 mm by moving the anode in and out of the cell along its axis.

To test the response of the detector, samples containing 30–150 ppm of a hydrogen were introduced using a Perkin-Elmer gas sample introduction system connected with a vacuum apparatus, provided with a mercury manometer. The detectors were operated at room temperature using as the carrier gas technical-grade argon, dried over molecular sieve 5A, at a flow-rate of 60 cm³/min. A 3-m column packed with molecular sieve 5A was used.

RESULTS AND DISCUSSION

Design I

The parallel-plate device does not detect hydrogen, and neither changes in the distance between the electrodes nor changes in the applied voltage improve the situation. Slight negative peaks (decrease in the ionization current) are observed after the injection of very large samples of hydrogen.

Design II

This device (essentially analogous to that reported previously¹) gives a sensitive response to hydrogen. The dependence of the sensitivity on the length and diameter of the anode is shown in Figs. 2 and 3. In all experiments the basic ionization current was $2 \cdot 10^{-7}$ A, i.e., the detector operated under conditions of considerable field excitation as the saturation "plateau" value was about $2.4 \cdot 10^{-8}$ A.

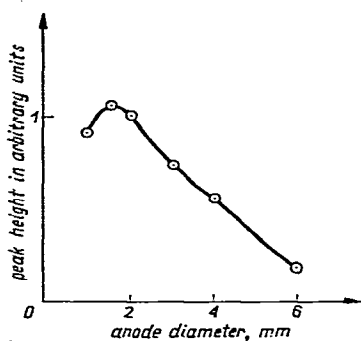


Fig. 2. Dependence of the height of the hydrogen peak (arbitrary units) on the diameter of the anode (anode length 8 mm) for detector II.

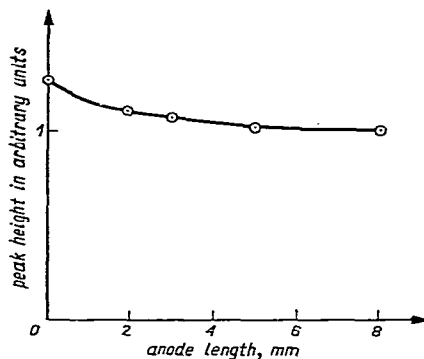


Fig. 3. Dependence of the height of the hydrogen peak (arbitrary units) on the length of the anode (anode diameter 2 mm) for detector II.

The optimal anode diameter with a length of 8 mm is 1.5–2 mm. Thinner electrodes fail to operate reliably, the noise level increases and long-period fluctuations in the ionization current develop. An electrode 2 mm in diameter was chosen for further experiments. The effects of the length of the electrode on the sensitivity of the detector is slight, as can be seen in Fig. 3. The highest sensitivity is obtained when the end of the electrode is at the level of the insulator ($l = 0$). Further increases in the electrode diameter up to 3.5 mm do not lower the sensitivity but result in a more stable background current.

The operating parameters of the detector equipped with a 3.5-mm diameter anode for $l = 0$ are summarized in Table I. Under the optimal conditions the detector is capable of considerable sensitivity (2.5-fold higher than that of our earlier device¹). The linear dynamic range is about 120, independent of the background current. The response of the detector was practically unchanged when a high positive voltage was applied to the anode, and a signal was collected from the cathode.

TABLE I

OPERATING PARAMETERS OF DETECTOR II (FIG. 1b)

Anode diameter = 3.5 mm; $l = 0$. U_a = anode voltage; $i_{det.}$ = ionization current.

U_a (V)	$i_{det.}$ (A)	Noise level (A)	Minimal detectable flow-rate of hydrogen (g/sec)	Sensitivity (C/g)
1920	$1.0 \cdot 10^{-7}$	$3.6 \cdot 10^{-11}$	$8.1 \cdot 10^{-11}$	0.9
2220	$2.0 \cdot 10^{-7}$	$5.0 \cdot 10^{-11}$	$5.0 \cdot 10^{-11}$	2.0
2400	$3.0 \cdot 10^{-7}$	$6.2 \cdot 10^{-11}$	$4.2 \cdot 10^{-11}$	2.95
2500	$4.2 \cdot 10^{-7}$	$8.0 \cdot 10^{-11}$	$3.8 \cdot 10^{-11}$	4.2
1750*	$2.1 \cdot 10^{-7}$	$5.0 \cdot 10^{-11}$	$1 \cdot 10^{-10}$	1.0

* Data from previous paper¹.

Design III

The current-voltage characteristics of this detector exhibit a plateau that has a pronounced slope (Fig. 4), possibly due to the formation of a space charge compensating the increment in the applied voltage. The dependence of the anode and grid

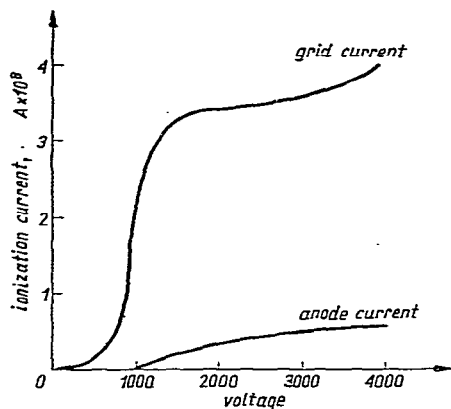


Fig. 4. Current-voltage curves for detector III (distance between grid and anode 9 mm).

currents on their distance apart at $U = 3900$ V is shown in Fig. 5. As expected, the grid current increases with an increase in distance at the expense of the anode current. The response of the triode to hydrogen was examined as a function of the distance between the grid and the anode both when the grid was earthed and the anode current was measured, and conversely when the anode was earthed and the grid current was measured. The cathode was set at a negative voltage. The results are shown in Fig. 6. The height of the hydrogen peak when the anode current is measured increases with increase in distance, but decreases when the grid current is measured.

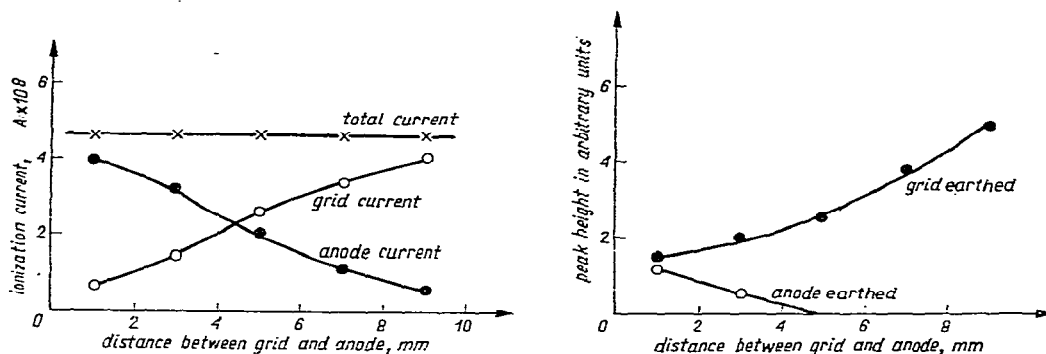


Fig. 5. Dependence of the grid and anode currents on the distance between the grid and anode at $U = 3900$ V.

Fig. 6. Dependence of the height of the hydrogen peak (arbitrary units) on the distance between the grid and anode. Upper curve; grid earthed, anode current measured; lower curve, anode earthed, grid current measured. $U = 3900$ V.

At greater distances (7 and 9 mm) either a lack of response or small negative peaks from the grid (tantamount to a decrease in current) are observed. Under optimal conditions ($U = 3900$ V, $l = 9$ mm, the grid earthed) the sensitivity is approximately 15-fold lower than that obtained with design II and is 0.25 C/g. However, owing to

the marked decrease in the noise level ($1.6 \cdot 10^{-12}$ A at a background current of $6 \cdot 10^{-9}$ A), the minimal detectable concentration of hydrogen increased to *ca.* $1.3 \cdot 10^{-11}$ g/sec. Changes in the supply system (a positive voltage applied to the anode, the cathode earthed) and complete reversal of the gas flow through the detector have only a slight effect on the operation of the device.

The present results, together with those previously reported¹, lead to the following conclusions:

(1) The source of radiation should be sufficiently active to ensure the high primary ionization of a gas, thus making it possible to obtain high background currents at relatively low electron multiplication when the likelihood of breakdown is negligible.

(2) The electrodes should be designed so as to produce a non-uniform field.

(3) The triode modification gives the best results in the detection of hydrogen owing to the low noise level at lower background currents.

The constructional details and operating parameters are similar to those of the well known Lovelock detectors², except for the use of a highly active radiation source.

Mechanism of operation

The detector gives a sensitive response to substances such as hydrogen (ionization potential, I.P., 15.43 eV), carbon monoxide (I.P. 14.01 eV), methane (I.P. 12.71 eV) and ethane (I.P. 11.5 eV); krypton (I.P. 14.0 eV) and xenon (I.P. 12.13 eV) give responses weaker by 2–3 orders of magnitude¹. The device fails to detect oxygen (I.P. 12.08 eV), nitrogen (I.P. 15.58 eV) and carbon dioxide (I.P. 13.79 eV).

Clearly, the energy of excited metastable argon atoms (11.6 eV) is insufficient to cause the occurrence of the well known Penning ionization:



A large increase in conductivity in the presence of comparatively small concentrations of hydrogen might be due to the occurrence of the reaction



However, the minimal energy of excited argon atoms (calculated using the heat of formation of the ArH^+ ion reported by Smith and Futrell³) should be as high as 14.2 eV. The presence of such highly energized species is possible; perhaps they are responsible for the weak signals observed for krypton and xenon, but this mechanism is of a little importance, as demonstrated by the lack of positive signals for oxygen and carbon dioxide. The high current density, the high energy of the electrons and the considerable concentration of excited argon atoms in the close vicinity of the anode seem to be decisive. Under such conditions the molecules will undergo decomposition. It is sufficient for an electron to have an energy in excess of 9 eV to make possible the occurrence of the reaction⁴



Even though the ionization potential of hydrogen atoms (13.6 eV) is much higher than

the energy of metastable argon atoms, the Hornbeck–Molnar process is energetically possible:



$$\Delta H = -186 \text{ kJ/mole } (-1.9 \text{ eV})$$

ArH^+ ions are well known from mass spectrometric experiments⁵. The occurrence of such a reaction agrees well with the observed increase in conductivity in the presence of hydrogen. The necessary concentration of transient metastable argon atoms and hydrogen atoms may be reached if the energy of the electrons and the current density are high enough. Apparently such phenomena can occur if the activity of the radiation source is sufficiently large.

The interaction of high-energy electrons and vacuum ultraviolet photons with gaseous methane, ethane and carbon monoxide raises them to the excited states, which have sufficient energy to cause them to decompose⁶; the products of decomposition are listed in Table II. The majority have ionization potentials less than the energy of metastable argon atoms and can be ionized; then the detector operates in a manner typical of the usual argon detectors. The products of decomposition of oxygen (O atoms, I.P. 13.62 eV), nitrogen (N atoms, I.P. 14.53 eV) and carbon dioxide (CO molecules, I.P. 14.01 eV) all have ionization potentials that are too large, and accordingly fail to give positive responses.

TABLE II

NEUTRAL PRODUCTS OF DISSOCIATION OF CH_4 , C_2H_6 AND CO

CH_4		C_2H_6		CO	
Product	I.P. (eV)	Product	I.P. (eV)	Product	I.P. (eV)
CH_3	9.84	C_2H_5	8.38	C	11.26
CH_2	10.4	C_2H_4	10.5	O	13.61
CH	11.13	C_2H_2	11.4		
H	13.6	CH_2	10.4		
		H	13.6		

The case of carbon dioxide deserves some explanation. The radiation stability of carbon dioxide is well established^{6,7}. However, this stability is only apparent. Carbon dioxide is decomposed but the initial decomposition products, carbon monoxide and oxygen, react to regenerate it. The steady-state concentration of the carbon monoxide is essentially proportional to (dose rate)^{1/2}; at the dose rates used in our experiments we would predict a steady-state concentration of carbon monoxide of the order of 50 ppm in pure carbon dioxide. Obviously, when carbon dioxide is present as a low-level additive, the concentration of carbon monoxide will be so small that the products originating from its secondary decomposition will not be detected. Thus, there is no contradiction in the fact that carbon dioxide does not respond, although its decomposition product is carbon monoxide, which does.

In conclusion, the positive signals given by hydrogen, carbon monoxide, methane and ethane originate from the reaction of metastable argon species with the

products of dissociation of these compounds, rather than from the direct ionization of compounds that have ionization potentials below 11.6 eV, as in the case with the usual argon detectors.

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