Journal of Chromatography, 151 (1978) 370–373

CHROM. 10,611

Note

Argon ionization detector sensitive to hydrogen

JANUSZ GAWŁOWSKI, JAN NIEDZIELSKI and ANDRZEJ WIĘCKOWSKI

Laboratory of Radiochemistry and Radiation Chemistry, Chemistry Department, Warsaw University, Żwirki i Wigury 101, 02-089 Warsaw (Poland)

(First received June 13th, 1977; revised manuscript received September 19th, 1977)

The argon ionization detector developed by Lovelock[1,2] in different versions, such as simple, micro and triode, in all of which argon is used as the carrier gas, is highly sensitive towards compounds that have ionization potential less than 11.7 eV. However, it has the disadvantage of responding poorly to methane and ethane, and not at all to other compounds with higher ionization potentials.

This paper describes the construction and performance of an argon detector with a high sensitivity towards hydrogen, carbon monoxide, methane and ethane.

EXPERIMENTAL

The simple cylindrical ion chamber shown in Fig. 1 is similar to Lovelock's argon detector[2], but with a much higher intensity tritium radiation source. The ion chamber, with a volume of about 1.2 ml, contains a titanium–^{3}H foil with an activity of 2 Ci in the form of a cylindrically shaped strip (30 × 10 mm), situated inside a cylindrical cathode, made from 10-mm I.D. stainless-steel tubing approximately 12 mm in length. The anode consists of a stainless-steel rod (O.D. 3 mm). The unit is made from readily available parts and can be dismantled and re-assembled easily.

The relationship between the applied potential and anode current with the ionization chamber filled with argon and air is shown in Fig. 2.

To test the response of the detector, samples containing 30–150 ppm of a compound to be measured were introduced using a Perkin-Elmer gas sample intro-

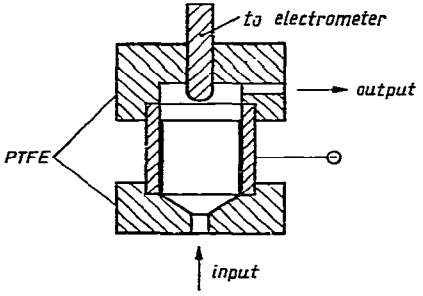

Fig. 1. Schematic diagram of argon ionization detector.

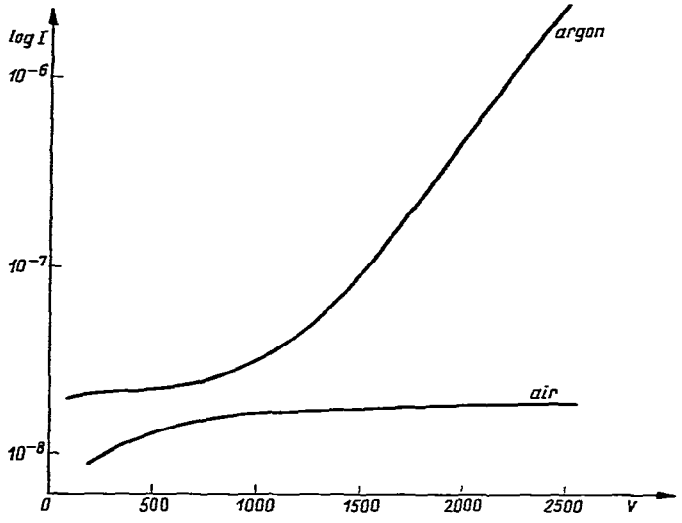

Fig. 2. Current–voltage curves for argon and air.

duction system, connected with a vacuum apparatus and provided with a mercury manometer. The detector was operated at room temperature using as the carrier gas technical-grade argon, dried over molecular sieve 5A, at a flow-rate of 60 ml/min. A 3 m × 5 mm I.D. column packed with molecular sieve 5A and a 2 m × 5 mm I.D. column packed with Porapak Q were used.

RESULTS AND DISCUSSIONS

We were interested mainly in the detection of hydrogen. An increase in ionization current due to the elution of hydrogen from the column is observed, beginning at a potential of about 700 V. The sensitivity of the detector increases with increase in the applied potential, as does the noise level (see Fig. 3). The following optimal operating conditions were obtained: potential, 1750 V; ionization current, $2.1 \cdot 10^{-7}$ A; noise level, $5 \cdot 10^{-11}$ A; sensitivity, 1 C/g; detection limit, $1 \cdot 10^{-10}$ g of hydrogen per second. At a flow-rate in the range 25–70 ml/min, the detector operates as a mass-flow sensitive detector (see Fig. 4). At higher flow-rates, the sensitivity decreases sharply. The reason for such behaviour is not clear, and it can only be stressed that Fig. 4 reflects the true behaviour of the detector as the decrease is not due to too slow a response time of the electronic equipment employed. The linear dynamic range is about 100. The dependence between the detector signal (S) and the mass of hydrogen (w) in a gaseous sample was found to obey the relationship

$$S = \frac{aw}{b+w}$$

where a and b are constants.

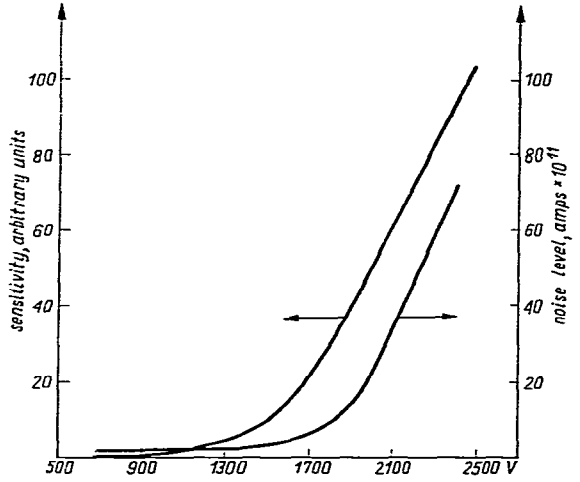

Fig. 3. Effect of voltage on detector sensitivity and noise level.

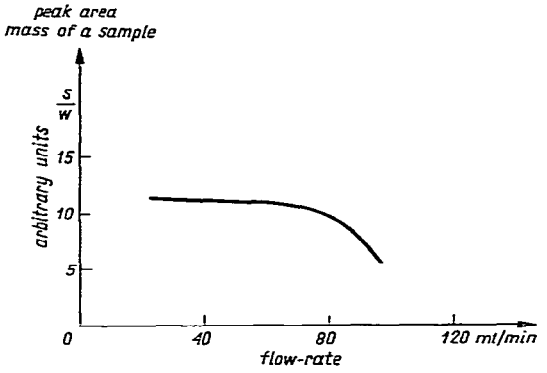

Fig. 4. Effect of flow-rate on sensitivity.

Under optimal operating conditions, changes in temperature in the range 25–50° and 10% changes in flow-rate have virtually no effect. The oxygen that is present in technical argon at concentrations up to 20 ppm has a slight effect, and water vapour causes a marked decrease in sensitivity. The purification of argon to remove trace amounts of oxygen by passing it trough a column filled with active copper at 220° resulted in an increase in sensitivity of about 20%.

We checked the response of the detector to other compounds with ionization potentials higher than the energy levels of the metastable states of argon. At potentials of 1700–2100 V, nitrogen, oxygen and carbon dioxide were found to decrease the ionization current, giving negative signals; the sensitivity is several orders of magnitude lower than that in hydrogen detection. However, carbon monoxide, methane and ethane give positive signals, the sensitivity towards carbon monoxide being comparable to that of hydrogen, and that towards methane and ethane being even higher. Xenon and krypton also give positive signals, the sensitivity being 2–3 orders of magnitude lower than for hydrogen, however.

The operating mechanism of the detector is not clear, and further studies to elucidate it should also result in further increases in sensitivity and linear range. It is worth noting that the range of applied potentials lies in the range of gaseous amplification, as can be seen by comparing the ionization current–voltage curves in Figs. 2 and 3. The high activity of the radiation source used in this device (*ca.* 20-fold higher than those normally used) is probably of great importance. Using a tritium source with an activity of 50 mCi we have obtained very weak positive signals at potentials exceeding 1800 V, the sensitivity being approximately two or three orders ofmagnitude lower than for detector equipment with a 2-Ci source.

Notwithstanding the uncertainty concerning the mechanism, the detector works well, and we have used it to determine trace amounts of hydrogen, carbon monoxide and hydrocarbons at levels down to 1 ppm.

ACKNOWLEDGEMENT

This work was partially supported by the Institute of Nuclear Research through Grant No. 3, 12. 02. 02.

REFERENCES

1 J. E. Lovelock, *J. Chromatogr.*, 1 (1958) 35.
2 J. E. Lovelock, in R. P. W. Scott (Editor), *Gas Chromatography 1960*, Academic Press, New York, 1961, p. 16.