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Radiofrequency detector for gas chromatography

PETER POPP*, SIBYLLE MOTHES and DETLEF HINNEBURG

Central Institute for Isotope and Radiation Research, Permoserstrasse 15, 7050 Leipzig (G.D.R.)

ABSTRACT

A radiofrequency detector is described that is designed as a parallel-plate ^{63}Ni electron-capture detector working with pure argon as carrier gas and with a radiofrequency voltage superimposed on a d.c. voltage. The principle of operation is that the radiofrequency voltage increases the mean electron energy within the detector, decreases the drift velocity and, owing to an increase in the recombination rate, the ionization current drops. In the presence of sample molecules the reverse process takes place: the drift velocity increases, the recombination rate decreases and the ionization current increases. Positive substance peaks occur. Detection limits down to 0.1 ppm for organic substances and 1.0 ppm for inorganic gases (carbon dioxide) are obtainable.

THEORETICAL

In 1967, Lovelock *et al.* [1] first described so-called electron attachment spectroscopy. A conventional electron-capture detector was driven in such a manner that a radiofrequency (rf) potential was impressed on the detector electrodes during the quiescent period between the collection pulses. As a result, the mean electron energy increased and substances with low thermal electron attachment cross-sections could be determined sensitively.

Popp and co-workers [2–4] modified this principle by superimposing a radio-frequency voltage (V_{rf}) on a d.c. voltage. This so-called rf electron-capture detection (rf-ECD) method was used especially for the analysis of halocarbons with low ECD responses (*e.g.*, chlorobenzene). Except for some experiments with argon–nitrogen mixtures [2], nitrogen was used as the carrier gas in all applications.

Fig. 1 shows that the superposition of an rf potential influences the shape of the current–voltage characteristics. Increasing V_{rf} values cause a decrease in the ionization currents. In early investigations it was found that the peaks of substances with low electron-capture cross-sections become positive if the radiofrequency voltage reaches 300–400 V. When argon (purity 99.999%) was used as the carrier gas, the decrease in the ionization current as a function of the superimposed rf potential was extreme (see Fig. 1) and there was an undesirable positive response for all substances with low electron-capture coefficients.

This effect led us to the idea of using this "disturbance" for the sensitive determination of such substances. The interpretation of this effect is simple: considering the dependence of the mean electron energy on the ratio of electric field strength and gas pressure (E/p value) given by Christophorou [5], it is evident that the
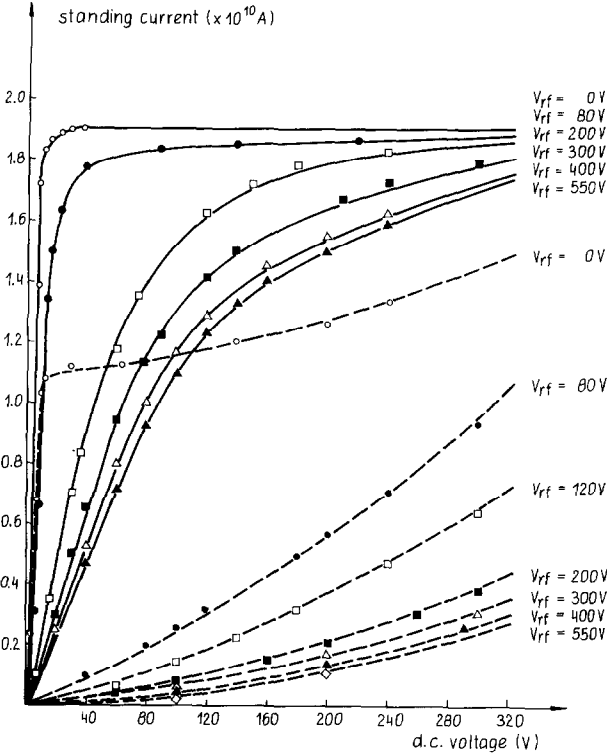
Fig. 1. Current–voltage characteristics for (solid lines) nitrogen and (dashed lines) argon as carrier gas.

mean energy increases with increase in E/p and then remains constant at about 0.9 eV for nitrogen and at about 5.5 eV for argon as carrier gas owing to the energy transfer by only elastic collisions. Let us consider the consequence for the ionization current. The connection between electron energy and drift velocity of the electrons under the influence of a d.c. field is given by

$$u = \frac{DneE}{p(\varepsilon_{\text{el}}^{5}/\varepsilon_{\text{gas}}^{5})} \tag{1}$$

where u is the drift velocity, D the diffusion coefficient for electrons, n the number of molecules/cm^3, E the electric field strength, p the gas pressure, $\varepsilon_{\text{el}}^{5}/\varepsilon_{\text{gas}}^{5}$ the ratio of the mean energies of electrons and carrier gas molecules and e the elementary charge. The superposition of an rf potential increases the electron energy, $\varepsilon_{\text{el}}^{5}$. The greater is the ratio $\varepsilon_{\text{el}}^{5}/\varepsilon_{\text{gas}}^{5}$, the lower is the drift velocity, u. Using argon as carrier gas the drift velocity decreases strongly and, as a result, the electron–ion recombination rate increases and the basic ionization current drops.

In the presence of sample molecules the reverse process takes place: the electron

energy, ε_{el}^5, decreases owing to inelastic collisions between electrons and sample molecules, the drift velocity, u, increases and the ionization current rises, so positive substance peaks occur.

This detection principle is usable for all compounds with low electron-capture cross-sections. For molecules with high thermal electron-capture cross-sections (*e.g.*, SF_6 and CCl_4) this mode of operation is unsuitable. Low concentrations of such molecules cause a decrease in the ionization current (electron capture dominates), whereas for higher concentrations the slowing down of electrons by inelastic scattering is also operative, causing peak splitting. The decrease in the mean electron energy is dependent on the energy absorption by the sample molecules. This explains why noble gas atoms (He) can be detected insensitively, molecules such as N_2 and H_2 more sensitively and organic molecules of low electron affinity with the highest sensitivity.

Although this detector uses the increase in electron mobility as an important part of its functioning principle, there are no analogies with the "indirect mobility detector" [6] or the "direct mobility detector" [7,8]. The principle of the "indirect mobility detector" is based on the decrease in the concentration of metastable excited noble gas atoms by sample molecules. In the "direct mobility detector" the charge carriers are collected by pulses and the increasing mobility of electrons in the presence of sample molecules also increases the ionization current. Whereas these mobility detectors mainly serve for the determination of inorganic gases, the rf detector can also be used for the detection of organic compounds of low flame ionization and ECD sensitivity (*e.g.*, CF_4 and C_2F_6).

EXPERIMENTAL

Fig. 2 shows schematically the parallel-plate rf detector with a ^{63}Ni source (activity 3.7×10^7 Bq). The electrode distance is 1 cm and the cell volume is about 300 μl. A voltage of $V_{eff} = 0-600$ V provided by an rf generator is superimposed on the d.c. voltage (0–450 V). The frequency of the alternating voltage is 30 MHz. The ionization current is measured by use of a vibrating reed electrometer.

The rf detector is part of a GCH 18.3/6 gas chromatograph (ZWG Chromatron). The gas chromatographic columns used were as follows: column A, 2 m × 3 mm I.D. glass, Chromosorb W AW DMCS (60–80 mesh; E. Merck, Darmstadt, F.R.G.) + 3% SE-30 (Varian Aerograph, Walnut Creek, CA, U.S.A.); column B, 2 m × 3 mm I.D. glass, Porapak QS (80–100 mesh; Waters Assoc., Milford, MA, U.S.A.); column C, 2 m × 3 mm I.D. glass, molecular sieve 5A (80–100 mesh; Jenapharm, Laborchemie Apolda, G.D.R.). The carrier gas was high-purity argon (99.999%) at a flow-rate of 50 cm³/min.

Low concentrations of gaseous compounds were produced by an exponential dilution flask; for gas sampling a three-port valve with a 1.0-ml sample loop was used. The hydrocarbons were diluted in *n*-nonane and injected with a 1-μl syringe.

RESULTS

Current–voltage characteristics in the presence of sample molecules
Fig. 3 shows the influence of carbon dioxide concentration on the shape of the current–voltage characteristics of the rf detector. Fig. 3a characterizes the rf-free case
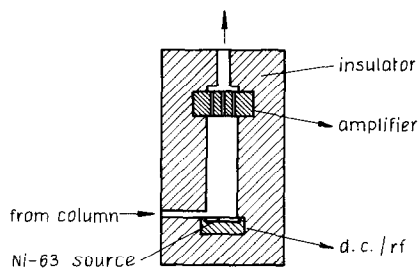
Fig. 2. Schematic diagram of the rf detector.

and Fig. 3b the current–voltage characteristics under the influence of an rf voltage of amplitude 120 V identical with that in Fig. 1b.

Fig. 3c is obtained if the argon carrier gas is replaced with an argon–500 ppm carbon dioxide mixture. The difference between curves c and b (*i.e.*, the increase in the ionization current) is given in Fig. 3d. It is shown that with the rf voltage of 120 V chosen for these investigations, voltages between 320 and 400 V provide the maximum signal. Such a maximum appears not only at an rf voltage of 120 V but also at any other V_{rf} value. However, for an rf voltage of 200 V d.c. voltages of about 500 V are necessary, and rf voltages > 200 V are unusable because the d.c. voltage necessary to reach the maximum increases rapidly. For V_{rf} values < 80 V the sensitivity of the detector (*i.e.*, the difference between the curves c and b in Fig. 3) decreases, so the optimum range of the rf voltage is between 80 and 120 V.
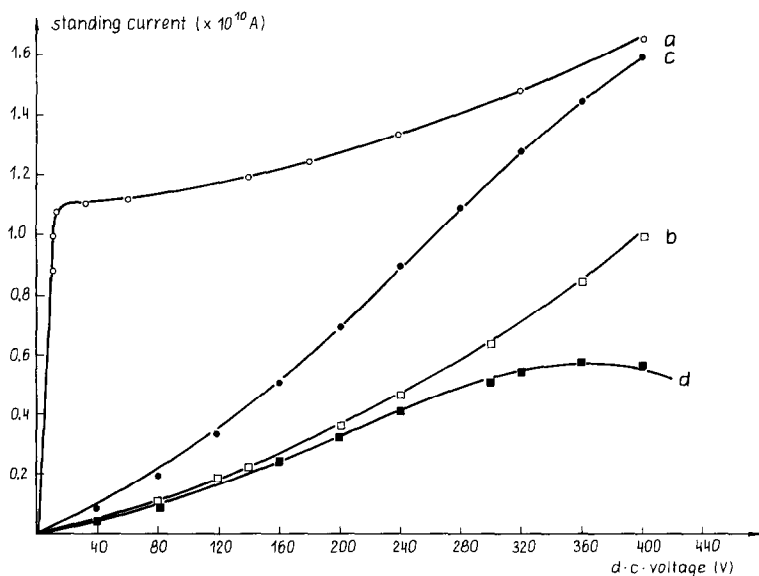

Fig. 3. Influence of a 500-ppm carbon dioxide concentration on the current–voltage characteristics of the rf detector. (a) Pure argon, rf amplitude 0 V; (b) pure argon, rf amplitude 120 V; (c) argon + 500 ppm carbon dioxide, rf amplitude 120 V; (d) difference between (c) and (b).

TABLE I

DETECTION LIMITS OF THE RADIOFREQUENCY DETECTOR FOR A NUMBER OF SUB-STANCES FOR A 1.0-ml SAMPLE AND A 10-s PEAK WIDTH

Substance	Column	Detection limit (ppm)	Oven temperature (°C)
Perfluorocarbons			
CF_4	B	5.0	25
C_2F_4	B	2.0	25
C_2F_6	B	0.4	25
C_3F_8	B	0.1	25
Hydrocarbons			
CH_4	C	5.0	25
C_6H_{14}	A	0.2	120
C_7H_{16}	A	0.1	120
C_8H_{18}	A	0.1	120
Permanent gases			
He	C	60.0	25
H_2	C	8.0	25
CO_2	C	1.0	100
CO	C	1.2	100

Detection limits and linear dynamic range

The detection limits of the rf detector for a number of organic and inorganic compounds were determined under optimum conditions (rf voltage 120 V; d.c. voltage 400 V). These values were calculated on the condition that a peak with a three-fold noise level is still detectable.

Table I gives the results for some perfluorocarbons, hydrocarbons and permanent gases. As described under Theoretical, the sensitivity of the rf detector is
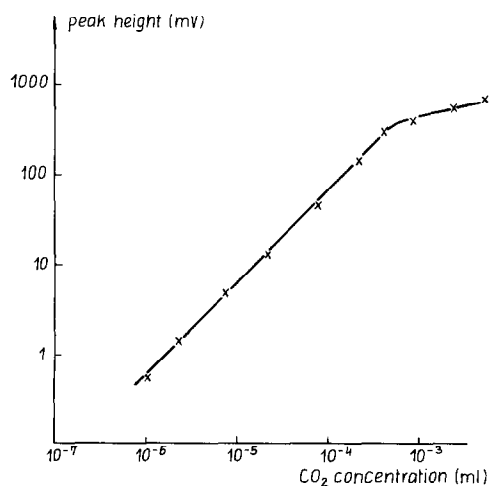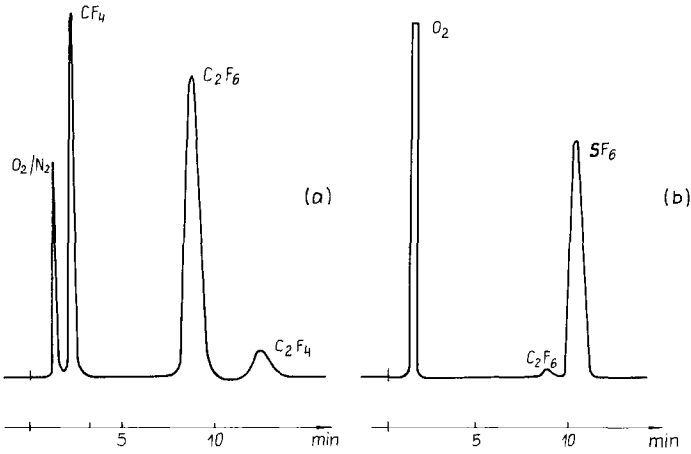

Fig. 4. Linearity for carbon dioxide.

Fig. 5. Analysis of a CF_4–C_2F_6–C_2F_4 mixture with (a) RFD and (b) cc-ECD. Conditions: column, B; d.c. voltage, 400 V; rf voltage, 120 V; temperature, 25°C; sample, 50 μl of gas mixture (40 μl of CF_4, 5 μl of C_2F_4, 5 μl of C_2F_6).

strongly dependent on the possibilities of energy absorption by the sample molecules or atoms.

Fig. 4 shows the linear dynamic range for carbon dioxide with an extent of 5 · 10^2.

Applications

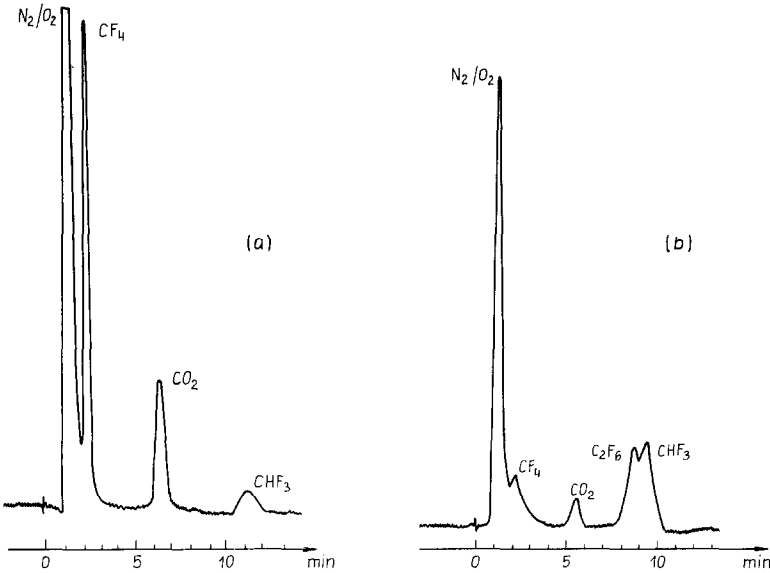Fig. 5 shows the analysis of a CF_4–C_2F_6–C_2F_4 mixture with rf detection (RFD)

Fig. 6. Analysis of products of (a) CF_4–CHF_3 plasma etching and (b) CHF_3 plasma etching. Conditions: column, B; temperature, 25°C; d.c. voltage, 400 V; rf voltage, 80 V; sample, 1 cm^3 of waste products of plasma etching.

and constant-current electron-capture detection (cc-ECD). RFD makes it possible to detect the CF_4, C_2F_6 and C_2F_4 concentrations, whereas cc-ECD gives only a small C_2F_6 peak and an extended peak for a ppb (10^9)-level impurity of SF_6.

Fig. 6 illustrates an application in microelectronics. When either ECD or flame ionization detection the chromatogram of the products of CF_4–CHF_3 and CHF_3 etching did not give CF_4, C_2F_6 and CO_2 concentrations, but with RFD it was possible to determine these substances. CO_2 is probably a decomposition product of COF_2 formed during the etching process.

CONCLUSION

These results indicate that RFD allows the sensitive determination of substances with low electron-capture cross-sections. Further investigations (influence of detector geometry, role of space charges) are necessary to optimize this procedure.

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