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CONCENTRATION CHARACTERISTICS OF THE HELIUM DETECTOR FOR GAS CHROMATOGRAPHY

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SUMMARY

The helium detector operated on N-55 type helium (5 ppm of total impurities) has a minimum in the ionization current for parts per million concentrations of H_2, Ar, N_2 and O_2. The fall in the current caused by H_2 is the largest and that caused by O_2 is the smallest and has not been previously reported. The size of the fall increases sharply with increase in the supply voltage. The addition of any impurity to the carrier gas decreases the minimum until it completely disappears at parts per million concentrations of the impurities added. The enhancement of ionization caused by the Penning effect takes place up to a certain limiting concentration, which varies from about 1300 ppm for H_2 to about 150 ppm for CO_2.

INTRODUCTION

The concentration characteristic, $I = f(C)$, of a chromatographic detector for a given component is the dependence of the detector ionization current, I, on the concentration of this component, C, in the carrier gas flowing in to the detector cell under fixed operating conditions, that is, excitation potential, temperature, pressure, flow-rate and purity of the carrier gas. This dependence should be linear to permit an easy evaluation of the concentration. However, often the concentration characteristic is linear only in a certain range, beyond which it can even be a non-monotonic function and cause abnormal chromatographic signals[1-5]. Anomalies with the helium detector have remained unexplained for a long time because on the one hand the role of the concentration characteristic in their formation has not been understood and on the other the influence of impurities has not been known. This has led to a low popularity and only rare use of the helium detector in spite of its high sensitivity and very good detection limits.

In this work the concentration characteristics of a helium detector run on pure N-55 type helium (99.9995 % purity) and on helium mixed with known trace additions of H_2, N_2, Ar or O_2 have been measured for H_2, N_2, Ar, O_2, CH_4 and CO. The measurements are interesting not only because of anomalies with the helium detector but also because they can contribute much to the elucidation of the mechanism of the ionization caused by beta particles in helium.

EXPERIMENTAL

Apparatus

A Carlo-Erba Model GH gas chromatograph[4] was used but the original detector was replaced with a Model DH-73 helium detector designed and built in the Laboratory of Chromatographic Detectors of the Institute of Nuclear Physics in Kraków. Its design is shown schematically in Fig. 1. The two parallel electrodes, 12 mm in diameter, were separated by a 1.8-mm PTFE insulator. One of the electrodes was a β-ray source consisting of a stainless-steel disc supporting 238 mCi of tritium absorbed on erbium. Gas concentrations for calibration were generated with a glass exponential dilution flask[6]. N-55 type helium was used as the carrier gas and purge gas. The supplier (l'Air Liquide, Lyon, France) specified the helium impurities in the catalogue attached to the cylinders as follows: O_2, 1; H_2O, 2; N_2, 2; H_2, 0.1; CH_4, 0.1; CO, 0.1; and CO_2, 0.1 ppm (by volume). However, according to the same catalogue, the total concentration of impurities did not exceed 5 ppm.
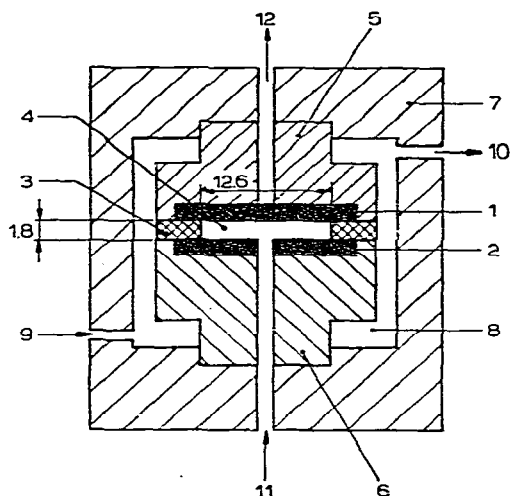

Fig. 1. Schematic diagram of the Model DH-73 helium ionization detector. 1 = Top electrode (β-ray source); 2 = bottom electrode; 3 = PTFE insulator between the electrodes; 4 = detector volume (ca. 0.2 cm³); 5 and 6 = electrode insulators; 7 = detector body; 8 = guard helium atmosphere; 9 and 10 = inlet and outlet for purging helium; 11 = carrier gas inlet; 12 = carrier gas outlet.

Impurities were added to the helium carrier gas and kept at a cetrain constant level by means of the permeation tube technique[7]. The permeation chamber manufactured and calibrated for this particular application has been described elsewhere[4,5]. The volume of samples injected was 3 cm³. The helium flow-rate through the detector was 1 cm³/sec. The gas chromatographic column used was a 2-m stainless-steel tube (5 mm I.D., 6 mm O.D.) filled with 40–80-mesh molecular sieve 13X. The temperature of the column was kept at 80° and the temperature of the detector and all other parts of the apparatus was ambient. The pneumatic circuit was made of stainless steel, including tubing and joint connections. After every disconnection of the carrier gas circuit or a break in the detector work it was necessary to clean the system for about 1 day in order to obtain optimal performance.

Methods for determining the concentration characteristic

The concentration characteristic can be obtained by the stationary method or the pulse method.

In the stationary method a number of mixtures of helium with the investigated component are prepared and each mixture is used as the carrier gas. Having constructed the voltage–current curve for each of the mixtures the concentration characteristic can be determined. Usually the diffusion chamber is used to produce the mixtures.

In the pulse method samples containing the investigated gas in known concentrations, C_d, are introduced into the pure carrier gas and the increments of the current at the tops of the peaks, ΔI_p, are measured. Ordinates of the concentration characteristic are calculated from the simple equation

$$I = I_b + \Delta I_p \tag{1}$$

where I_b is the basic current. The concentrations corresponding to these values of the current can be found from the equation

$$C_p = \frac{C_d V_d}{t_h U} \tag{2}$$

when the carrier gas is free from the analysed component, and if it is not, from the more general equation

$$C_p = C_0 + \frac{(C_d - C_{01}) V_d}{t_h u} \tag{3}$$

where

C_{01} = constant concentration of the analysed component present in the carrier gas as an impurity at the injection point;

V_d = volume of sample injected;

t_h = half-width of the peak;

u = volume flow-rate of the carrier gas.

Eqns. 2 and 3 are valid under the assumption that chromatographic elution curves are symmetrical and that their shapes can be approximated by a triangle.

The pulse method was mainly used in this work. The samples were taken from the exponential dilution flask and injected into the carrier gas at intervals equivalent to the time constant of dilution for the flask. Because of the low frequency of injections and the approximate validity of eqns. 2 and 3, the concentration characteristics obtained in this way are not too precise and the curves shown below serve only to illustrate the character of changes in the ionization current of the helium detector with the admixture added.

RESULTS AND DISCUSSION

The concentration characteristics of the helium detector can have two different shapes, which are shown in Fig. 2a for H_2 and in Fig. 2b for CO. The minimum at C
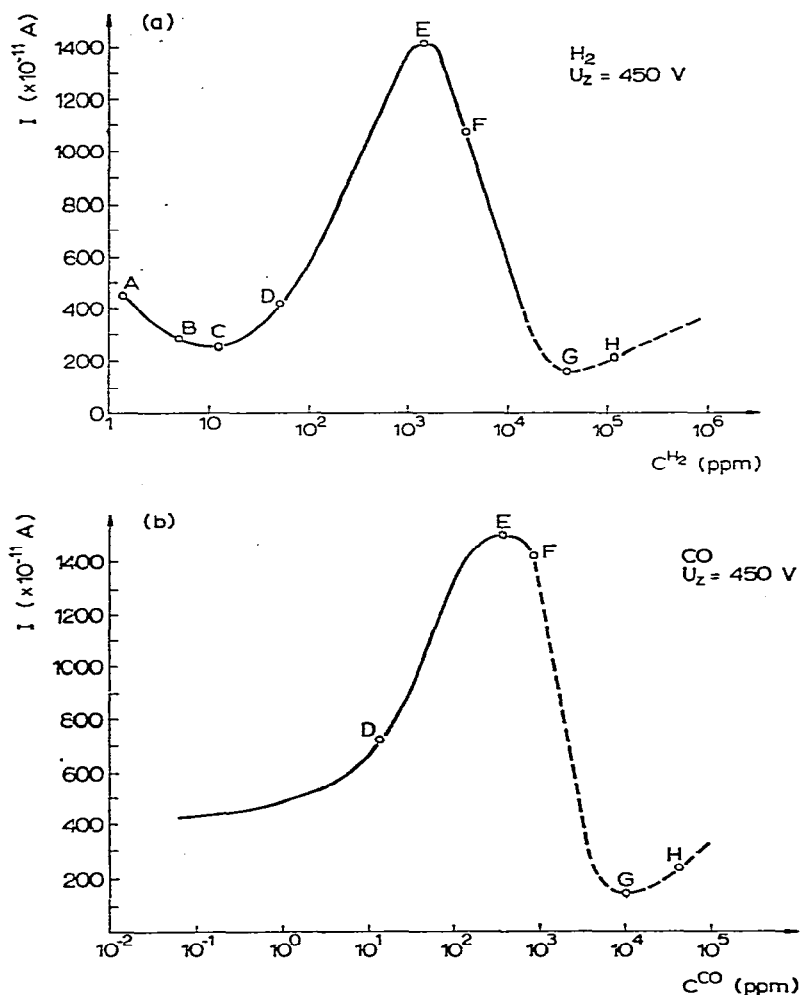
Fig. 2. Concentration characteristic, $I = f(C)$, of the He detector (a) for H_2 and (b) for CO. Carrier gas, N-55 type helium; flow-rate, 1 cm³/sec; supply voltage, $U_z = 450$ V; electrode distance, $d = 1.8$ mm; radioactive source, 238 mCi ³H/Er; chromatographic column, molecular sieve 13X, 2 m long, at 90°; detector temperature, 20°.

and the maximum at E demand special consideration. The range between points C and E is called the Penning range.

Initial minimum for small concentrations

The decrease in the concentration characteristic for very small concentrations was observed for only four components: H_2, Ar, N_2 and O_2, as shown in Fig. 3. Previously this effect was reported for H_2, Ar and N_2 by Parkinson and Wilson[2,3] and for H_2 by Poy and Verga[4].

The fall in the current, $\Delta I_{min.}$, at the minimum point C, given by the equation

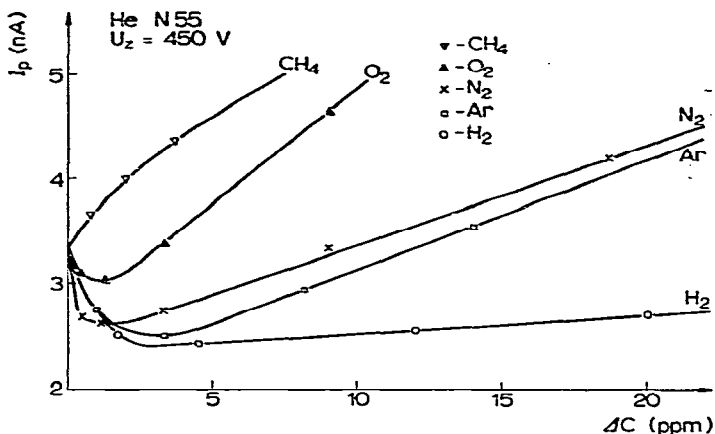$$\Delta I_{min.} = I_b - I_{min.} \tag{4}$$

Fig. 3. Variation in helium detector current *versus* concentrations of H_2, Ar, N_2, O_2 and CH_4 for N-55 type helium as carrier gas. Operating conditions as in Fig. 2.

where $I_{min.}$ is the lowest current at point C on the curve in Fig. 2a, was found to be greatest for H_2 and smallest for O_2. Admixture of every other gas to the helium reduces the fall in current, $\Delta I_{min.}$, and above a certain impurity level the minimum disappears for all four gases. It was noticed that the initial fall of the detector current is removed by adding about 25 ppm of H_2, 10 ppm of O_2, 15 ppm of N_2 or 5 ppm of Ar to the N-55 type helium carrier gas by means of the diffusion chamber. As the impurity level is increased the initial fall in current disappears first for O_2 and then for N_2, Ar and finally H_2. Fig. 4 shows the initial parts of the concentration characteristics obtained for the same gases as in Fig. 3 but with the detector supplied with N-55 type helium containing 35 ppm of H_2.

The concentration, $C_{min.}$, at which the detector current is at a minimum can be read from the concentration characteristic. However, it was found that the value of $C_{min.}$ for H_2 depended on the method of measuring it. Concentration characteristics
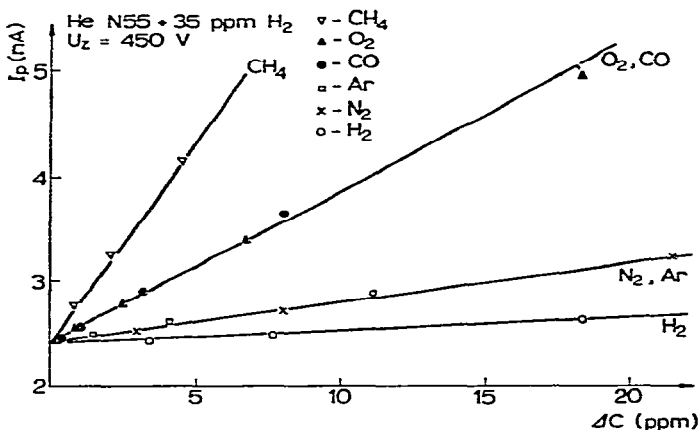

Fig. 4. Variation in helium detector current *versus* concentration of H_2, Ar, N_2, O_2, CO and CH_4 for N-55 type helium mixed with 35 ppm of H_2 as the carrier gas. Other conditions as in Fig. 2.

for H_2 obtained by three different methods are shown in Fig. 5. Although the values of $I_{min.}$ are virtually identical, the values of $C_{min.}$ differ considerably, being 5 ppm by the pulse method with the exponential dilution flask, 20 ppm by the pulse method with the diffusion chamber used to generate the concentrations needed and 30 ppm by the stationary method. These differences are not understood and they cannot be attributed to experimental errors only. They were found only for H_2.
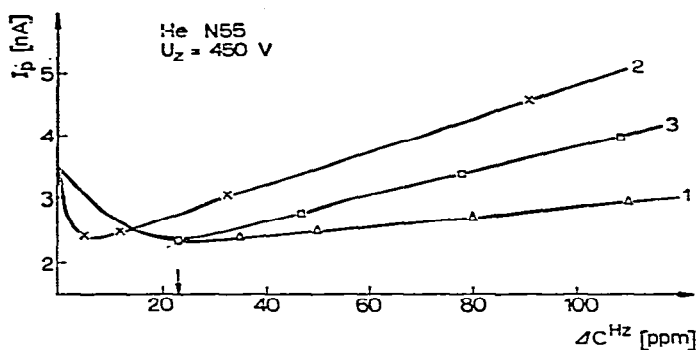

Fig. 5. Initial part of the concentration characteristic of the helium detector for H_2 obtained by (1) stationary method, (2) pulse method with the exponential dilution flask and (3) pulse method with the diffusion chamber.

The fall in the current, $\Delta I_{min.}$, depends strongly on the supply voltage, as illustrated in Fig. 6. The dependence of the detector basic current, I_b, on the voltage and the ratio $\Delta I_{min.}/I_b$ are also indicated in Fig. 6. For the voltage from the plateau of the voltage–current curve, $\Delta I_{min.}$ is distinguishable from the noise level for H_2 and Ar only. It can be seen from Fig. 6 that from 250 V $\Delta I_{min.}$ increases exponentially at a greater rate than the basic current, I_b, for pure N-55 type helium.

The value of $C_{min.}$ was found to be independent of the voltage in the tested range.

The reasons for the initial fall in the ionization current with the addition of parts per million amounts of H_2, Ar, N_2 or O_2 into the N-55 type helium carrier gas have not yet been elucidated. Some hypotheses that had been made by a few authors[1,2,8] in the past were summarized elsewhere[9]. Further investigations are needed in order to achieve a full understanding of that phenomenon.

The minimum of the concentration characteristic at point C has the disadvantage that it causes abnormal responses of the helium detector, but it can also play a positive role as an indication that the purity of a batch of helium carrier gas is sufficiently high that its further purification is not necessary. The possibility of the utilization of this phenomenon for the detection of hydrogen with a 10-fold higher sensitivity than the normal positive range of the He detector was first indicated by Parkinson and Wilson[2]. It can be seen from Fig. 7 that the sensitivity of the helium detector run on pure N-55 type helium in the negative mode is a few times better for O_2 and N_2 than the sensitivity of the detector in the positive mode after adding 35 ppm of H_2 to the carrier gas.
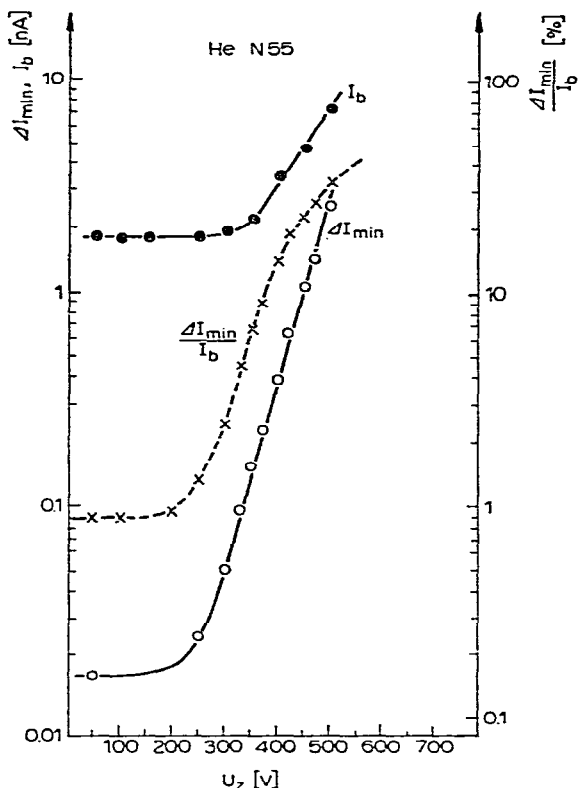
Fig. 6. Dependence of $\Delta I_{min.}$ on the supply voltage for H_2 and the ratio of $\Delta I_{min.}$ to the standing current, I_b.

Penning range

When all factors are constant, the ionization current of the helium detector between points C and E increases with addition of the test compound to the carrier gas until the maximum value, $I_{max.}$, is reached. This enhancement of the ionization is caused by the Penning effect and the differences in sensitivity for various gases are well known[1,4,10] and understood[8]. Most often just the detector operating in this range is referred to as the helium detector and is used as such in quantitative analysis.

The concentration characteristic, $I = f(C)$, does not depend directly on the carrier gas flow-rate but it does depend on it indirectly, owing to the changes in pressure inside the detector cell and to a change in the amount of impurities introduced through small leaks and diffusion into the system. An increase in the pressure decreases the current. The assertions concerning the influence of the flow-rate and pressure are valid for the whole concentration characteristic.

The sensitivity of the helium detector decreases with increase in the impurity level; however, the addition of parts per million amounts of hydrogen to N-55 type helium can slightly improve it. The deterioration of the sensitivity depends not only on the concentration of impurities but also on their type. The addition of CO_2, CO, O_2 or other gases for which the cross-section for the Penning effect is large is more harmful than the addition of H_2, for which this cross-section is the smallest.
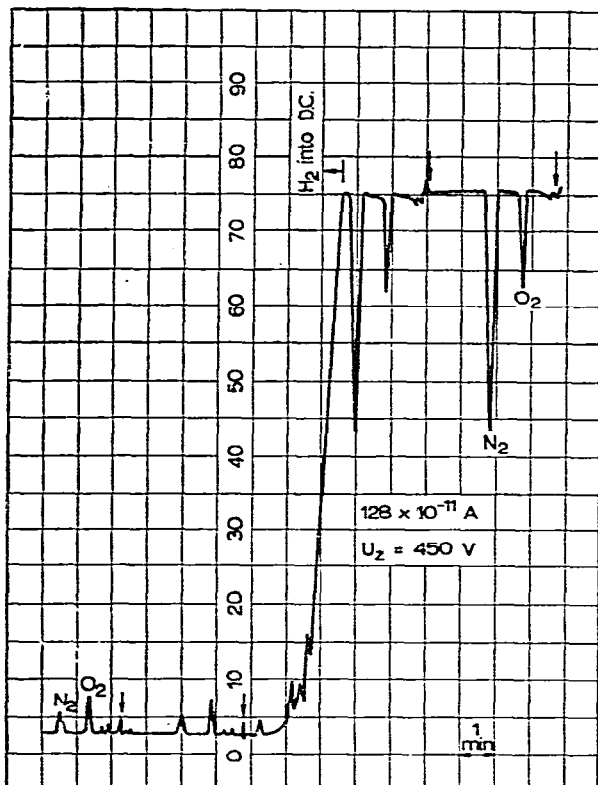
Fig. 7. Effect of the addition of 35 ppm of H_2 to N-55 type helium carrier gas on the standing current and the polarity and magnitude of the detector signal for O_2 and N_2.

The maximum of the concentration characteristic

The maximum increment of the helium detector current, $\Delta I_{max.}$, given by the equation

$$\Delta I_{max.} = I_{max.} - I_b \tag{5}$$

where $I_{max.}$ is the highest value of the current at point E, does not depend on excitation potential up to about 300 V. Above this value it increases first exponentially and then faster until a current breakdown, which takes place between 470 and 500 V depending on the compound being tested. Because electrical breakdowns in the helium detector can be damaging, the supply voltage should not exceed 450 V.

For voltages up to about 300 V the detector current does not fall with further addition of the test compound after reaching the maximum value, but levels off. The value of $\Delta I_{max.}$ varies with the compound being tested.

As the impurity level of the carrier gas increases, the value of $I_{max.}$ decreases. A 30% decrease in $I_{max.}$ was observed after addition of about 18 ppm of O_2 to the N-55 helium carrier gas.

The value of the concentration, $C_{max.}$, for which the current reaches a maximum for a given compound is a limiting value. If the impurity content of the carrier

gas is equal to or higher than this value, the detector responds with negative peaks to all of the eluted components. On the other hand, the closer the impurity level of the carrier gas approaches the limiting value, the smaller is the usable range of the detector for the analysis of samples.

Table I gives values of $C_{max.}$ evaluated by means of eqn. 2 on the basis of the data obtained during calibration of the detector at 450 V. The values of $C_{max.}$ evaluated by Berry[1], Wiseman[11] and Karmen et al.[12] are also quoted. These workers used a detector with cylindrical electrodes but did not mention the values of the supply voltage.

TABLE I

LIMITING CONCENTRATIONS ($C_{max.}$) IN N-55 TYPE HELIUM

Component	Concentration (ppm by volume)			
	Present measurements	Berry[1]	Wiseman[11]	Karmen et al.[12]
H_2	1300	1500	1000	—
Ar	850	1000	170	960
O_2	350	400	250	280
N_2	700	800	750	520
CH_4	400	590	100	—
CO	450	300	—	—
CO_2	150	100	170	80
H_2O	—	50	—	—

The differences between the values in Table I probably stem from differences in the contamination of the helium carrier gas used and from differences in the supply voltages. The effect of impurities is additive so that combination of impurities reduces the individual values of $C_{max.}$. $C_{max.}$ decreases slightly as the supply voltage increases. Another possible explanation is that the other workers might have evaluated the limiting concentrations in a different way.

Whatever the differences, the common factor about the values in Table I is the highest value of $C_{max.}$ for hydrogen and the lowest for CO_2 (or H_2O in one instance). Large differences between one component and another make it evident how important the composition of helium impurities is for the proper operation of the helium detector.

The $C_{max.}$ values are the upper limits of concentrations of samples analysed in the positive and monotonic range of the helium detector. For excitation potentials higher than the critical value the upper limit establishes the concentration at which the electrical breakdown occurs; the higher the voltage, the lower is this concentration.

Concentration characteristic above $C_{max.}$

The mechanism of the fall in current for concentrations higher than $C_{max.}$ has not yet been explained. It is probable that this fall is caused by the moderation of the electrons in inelastic collisions with the added molecules to such an energy level that the excitation of helium atoms to metastable states becomes impossible.

It seems that the range of the concentration characteristic between points E

and G in which the current drops could be used for quantitative analysis, but further investigations are needed.

At point G the function changes its character to a rising curve and further increases in the concentration of additives cause an increase in the current, as the detector begins to work as a cross-section detector in the gas amplified region.

CONCLUSION

The results obtained indicate that the helium carrier gas should not be too pure and should contain small amounts of impurities in order to remove the initial minimum and make the function rise monotonically to a limiting concentration beyond which the detector current begins to fall. The limiting concentrations range from about 150 ppm for CO_2 to about 1300 ppm for H_2. If the contamination of the helium carrier gas exceeds the limiting value for a given component, the ionization current decreases with the addition of any other component and it becomes impossible to run the detector in the positive range.

These results create a basis for a better understanding of the anomalous signals of the helium detector[13]. They also contribute to a further explanation of secondary processes that occur in slightly contaminated helium ionized with beta particles and standing behind the extremes of the helium detector concentration characteristics.

REFERENCES

1 R. Berry, in M. van Swaay (Editor), *Gas Chromatography 1962*, Butterworths, London, 1962, p. 321.
2 R. T. Parkinson and R. E. Wilson, *J. Chromatogr.*, 24 (1966) 412.
3 R. T. Parkinson and R. E. Wilson, *J. Chromatogr.*, 37 (1968) 310.
4 F. Poy and R. Verga, *Characteristics and Performance of a New Helium Ionization Detector GC System*, Carlo Erba, Milan, 1970.
5 J. Lasa and E. Broś, *J. Chromatogr. Sci.*, 12 (1974) 807.
6 J. E. Lovelock, *Anal. Chem.*, 33 (1961) 162.
7 A. N. O'Keeffe and G. C. Ortman, *Anal. Chem.*, 38 (1966) 760.
8 E. Broś and J. Lasa, *J. Chromatogr.*, 94 (1974) 13.
9 E. Broś, *Ph.D. Thesis*, University of Mining and Metallurgy, Kraków, 1975.
10 C. H. Hartman and K. P. Dimick, *J. Gas Chromatogr.*, 4 (1966) 163.
11 W. A. Wiseman, *Nature (London)*, 192 (1961) 964.
12 W. A. Karmen, L. Giuffrida and R. L. Bowman, *Nature (London)*, 191 (1961) 906.
13 E. Broś and J. Lasa, in preparation.