A NEW DETECTOR FOR A GAS CHROMATOGRAPH USING ELECTRON CURRENT FOLLOWING GLOW DISCHARGE

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When a flowing gas sample containing N_2O is luminously discharged at a low pressure, a "Nachleuchten" or afterglow is observed at the portion distal to the discharge electrodes. MOCHIZUKI and others¹⁾ have utilized this afterglow to analyse N_2O by determining the relationship between the light intensity of the glow and the concentration of N_2O . In connection with this, the present authors measured the space charges along the discharge tubing, using LANGMUIR's single collector electrode²⁾. The first aim of the measurement was to determine whether the afterglow was produced by some specific combination of positive and negative ions, or positive ions and electrons. However, no such combination was observed, but the change in the electron current in pure N_2 was confirmed by mixing small amounts of other gases such as N_2O , O_2 and CO_2 . The results of this study inspired further investigation to determine whether this method is applicable as a detector in gas chromatography.

Hitherto many ionization methods have been used as detectors in gas chromatography^{3,4)}. Most of them have measured the ion currents in accelerating electric fields, however, the present method measures the electron current which follows the luminous discharge without applying any electric fields. The results obtained are fairly reproducible and no complicated and expensive equipment is required.

METHOD

The apparatus consists of two parts, a chromatographic column and a detector as illustrated in FIG. 1. The detector is similar to the discharge tube reported in a previous paper concerning N_2O analysis¹⁾ except for three collector electrodes. These collector electrodes are sealed at 5 cm intervals, in the distal portion of the discharge electrodes. Each electrode is a ring of 0.3 mm Pt wire, set in a glass tube

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FIG. 1. Diagram of the apparatus.

(I.D. 4 mm). They are grounded through high resistors (10^8 to 10^{10} ohms).

The column is composed of a glass tube (I.D. 4 mm) filled with activated charcoal (60-80 mesh). A constant temperature was maintained in the column by circulating heated water (50 to 75°C). In order to secure a constant sample volume, a bypass for the carrier gas was set at the inlet of the column.

The electrode potential was measured by an electrometer (Takeda Riken Co. Tokyo) using a vibrating capacity method. The discharge tube was exposed to room temperature, the vacuum pressure was set at 4 mmHg, and the flow rate of the carrier gas at 20 ml per min.

RESULTS

The electrode potential varied greatly with the resistance through which the electron current was led to the ground. When the resistance was higher than 10^{10} ohms, the electrode potential was unstable and also required a slow response time. Therefore, both 10^8 and 10^{10} ohm resistors were used in most of the experiments.

The actual record shown in FIG. 2 was obtained when 2 ml of a gas mixture of about 20% O_2 , 5% CO_2 , 40% N_2O and 35% N_2 was carried with N_2 through a 20 cm column. This curve was recorded through an electrode 15 cm from the discharge electrode and through a 10^8 resistor. Successive peaks of O_2 , CO_2 and N_2O appeared on the curve. The peak heights were influenced by many factors such as the flow rate, the vacuum pressure, the discharge voltage, and the distance between the collector and the discharge electrode.

FIG. 2. An actual record of a gas mixture containing O_2 , CO_2 and N_2O .
 Carrier: N_2 , Column: Activated Charcoal 20 cm, Temperature: $50^\circ C$,
 Flow: 20 ml/min, Vacuum Pressure: 4 mmHg.

However, when these factors were kept constant, the peak height was stable and was proportional to the concentration of the test gas.

FIG. 3 and 4 show the calibration curves for peak O_2 and CO_2 potentials plotted against their concentrations as measured by SCHOLANDER's apparatus. These three curves were obtained through three different collector electrodes. The O_2 peak potentials decreased exponentially with an increase in the distance between the discharge and collector electrodes. When this distance was 5 cm, the electron current was about 5 times greater than when this distance was 10 cm. In every case, the O_2 calibration curves showed gradual decreases as the O_2 concentration increased. On the other hand, the CO_2 peak potentials decreased as the collector electrodes approached the discharge electrodes. No peak such as is shown in FIG. 2 was actually observed at the first electrode. As may be seen in FIG. 4, the ratio of peak heights at the second electrode to those at the third, was not as large for CO_2 as it was for O_2 .

When the resistance was 10^{10} ohms, the peak potentials were about 100 times greater than those at 10^8 ohms. However, the calibration curve changed for the worse, probably because of the potential change in the collector electrode produced by the electron current.

FIG. 3. O₂ calibration curve.

FIG. 4. CO₂ calibration curve.

DISCUSSION

Investigation of the space charge in plasma was first reported by LANGMUIR and MOTT-SMITH in 1924. They observed the electron and the ion currents by inserting a single collector electrode in a discharging fields. As is described in their report, because of the small mass and consequent high mobility of electrons, electron current densities in uniformly ionized gases may be hundreds of times greater than the positive ion current densities. In the present study, the collector electrode was simply leaked to the ground through a 10^8 ohm resistor, and no voltage was applied to it, therefore, the observed current must be roughly equal to the electron current.

The method utilizing the luminous discharge had already been developed by PICKETHLY in 1958⁵⁾. His method is based on the principle that the discharge current depended upon the concentration of test gas at a constant discharge voltage. According to LOVELOCK³⁾, in this method, the organic compounds are decomposed to their constituent elements when discharged, and the deposition of carbon on the surface of the cathode following such decomposition can profoundly alter its emission of electrons. However, in the present method, the discharge electrodes are set outside the glass tube, and the collector electrode is away from the discharge electrode. Therefore, the alteration of sensitivity will be greatly improved, even for measurements of organic compounds. Since no applied voltage to the collector electrode is required, the apparatus is more simple than PICKETHLY'S.

At present, it is certainly not clear, whether the change in the electron current is produced by the capture of electrons by some test gas, or by a net change in the number of electrons in the discharge field. As has already been described, the CO_2 peak disappeared at the first electrode, and the greatest peak was seen at the second electrode. Therefore, as far as CO_2 is concerned, the peak may have been produced by the capture of electrons by CO_2 molecules during travel from the discharge portion to the collector electrode.

Although the O_2 calibration curve was not linear, as is shown in Fig. 3, it will attain linear characteristics, if the sample volume is reduced from 2 ml to somewhat less. Furthermore, this has the following two advantages: the CO_2 peak appears on the opposite side of the O_2 on the recorded curves, and N_2 can be used as a carrier gas for the O_2 determination. Therefore, this method may be useful in analysis of respiratory gases.

SUMMARY

From the fact that the electron current following a glow discharge of N_2 was markedly influenced by mixing a small amount of other gases, a new

detector for a gas chromatograph was designed. The glow discharge was generated by applying $2-3 \times 10^3$ V of 1 Mcps from outside the glass discharge tube.

The electron current was measured through three single collector electrodes sealed at different positions, 5, 10 and 15 cm distant from the discharge electrodes. The detector was sensitive to both O_2 and CO_2 , and their peaks appeared on opposite sides of the N_2 level.

Since N_2 gas may be used as the carrier gas, and the structure of the equipment is very simple, this detector may be very useful in analysis of respiratory gases.

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