QUICK ANALYSIS OF GASEOUS MIXTURES BY ISOTHERM GASCHROMATOGRAPHY FOR COMPONENTS OF VERY DIFFERENT RETENTION CHARACTERISTICS

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In the gas-chromatographic analyses of gas-mixtures produced in the conversion of methane by air or by water vapour, or obtained from generators and burners, a frequent problem arises by the fact that there is a great difference between the retention factors of carbondioxide and the so-called permanent gases. Using only a single column the analysis becomes time consuming or otherwise two analyses are needed, unless the problem is solved by switching the carrier gas stream containing the sample in between the two columns during each analysis which is a rather cumbersome procedure. Poli and Taylor [4] applied a system of two columns and two detectors while Bennett, Martin and Martinez [1] used temperature programming in a single column — single detector system for the solution of the problem. In Madison's apparatus [2] two columns and one detector are used with temperature programming. These approaches are somewhat complicated. A similar but also problematic solution is to divide the column into two parts and to separate the component with the great retention factor by leading it through a separate connection directly to the detector. The component is taken from the end of the frontal part of the column by operating the stopcock soon after the sample has been introduced and the other components are separated. These components with smaller retention factors are either being accumulated in the second part of the column or are carried away in another carrier gas stream. When the components with high retention factors have passed the detector the subsequent operation of the stopcock leads the components into the second part of the column to the detector. This procedure provides significant reduction in time, but it is considered to be disadvantageous because of the double operation of the stopcock. Manka [3] uses two columns connected in series inserting a delaying column. The "hot wire" detector has one of its cells between the columns connected in series while its second cell is situated at the end of the second column. By this method it is possible to effect an analysis without altering the position of the stopcock within a short period (it might be necessary to reverse the polarity of the measuring bridge circuit during the analysis).

Independently of MANKA we have worked out a rather similar method to solve the above problem and our method is faster than that of MANKA by reducing his quoted analysis times by a factor of four.

Our method was worked out for samples of the gases: H_2, CH_4, CO, CO_2, O_2 and N_2, but it can be applied with the appropriate modifications in each case when there is a component or components of high retention factor among others with low retention level and when it is possible to remove selectively and quantitatively the high retention components from the carrier gas by a trap which does not enter into irreversible reactions with the more mobile components. There are two different points in our method with respect to that of MANKA. This author uses argon as carrier gas in order to be able to analyze H_2. This method has an adverse effect on the sensitivity of the "hot wire" detector towards other components. To prepare a calibration for quantitative evaluation it is always necessary to use gas mixtures of those gases which are to be determined. (It is important to mix the components thoroughly which might prove to be surprisingly difficult.) In case the gas mixtures for calibration contain variable portions of hydrogen then using constant sample volumes, it is possible to determine the hydrogen content even in those cases when the carrier gas itself is hydrogen. Determination of hydrogen from the amount of the other components naturally carries a higher error margin than that of the direct chromatographic analysis of H_2. Using hydrogen as carrier gas, however considerably improves the precision and sensitivity of the determination of the other components in "hot wire" detectors which, in our opinion, more than compensates the error mentioned above.

Flow design

Fig. 1 is the flow diagram of the analytical procedure:

The two detector-cells form the nearby arms of a Wheatstone bridge. The sample for analysis goes through the following processes. When passing through the sampling device towards column 2, the heavy components are separated from the rest of the sample as well as from each other. All components pass through detector-cell 3 and give rise to appropriate signals. Since the heavy components are well separated on column 2, their quantity can be determined from the corresponding chromatographic peaks. Therefrom the gas stream enters absorbing column 4, where the heavy components are finally separated from the gas stream. The other components enter column 5 in which the lighter ones are separated and upon reaching detector 6 they produce deflection on the recorder in an opposite direction than in the previous phase of the measurements. As compared to MANKA's system the present arrangement obviously shortens the analysis time since it is not necessary

to wait until the heavy components pass through the column for separating the lighter ones. This time always predominates in such analyses. The columns should be so designed that the component with the smaller retention time should not appear in detector 6 until the heaviest component leaves detector 3. The polarity of the measuring bridge can be altered between the two series of chromatographic signals if necessary in order to get deflections in the same direction. This is not absolutely necessary when the recording paper has
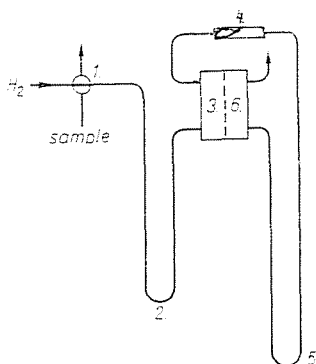

Fig. 1

1.: sampling device *2.*: column I *3.*: detector-cell *4.*: absorption column *5.*: column II *6.*: detector-cell

enough width; in such a case the base-line can be set to the middle of the chart or otherwise according to the signal magnitudes expected.

In the following details are given of a system used to analyze samples composed of O_2, CO_2, CH_4 and CO gases.

Apparatus

The volume of sampler 1 is 0.95 ml, column 2 is filled with activated charcoal of grain size 0.2 mm, type "Nuxit A" wetted by 30% glycerol. The length of column 2 is 30 cm, its internal diameter is 4 mm, while detector-cells 3 and 6 have lengths of 60 mm and their internal diameter is 4 mm. In the detectors there are tungsten wires of 0.030 mm diameter. Absorbing column 4 is 100 mm long with an internal diameter of 5 mm filled with solid KOH. Column 5 has diameter of 6 mm and length of 130 cm, its content being activated charcoal, type "Nuxit A" of grain size 0.2—0.3 mm wetted by 3% glycerol. The carrier gas speed (hydrogen) is 93 ml/minute, input voltage of the Wheatstone bridge is 4.1 V, as recorder a self-balancing potentiometer of type MAW with full scale deflection of 2 mV is used.

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Results

A typical chromatogram is shown in Fig. 2. The time of the analysis is 3 minutes and its relative error is $\pm 3\%$ for a component. No temperature control is necessary, the columns and detector-cells work at room temperature.

When the heavy substances are alcohols then as absorbing material $CaCl_2$ can be used in column 4. It has been proved that alcohols adsorbed on $CaCl_2$ do not dissolve gases to a significant amount, neither acetylene nor carbondioxide, for example. It is possible, of course, to separate permanent
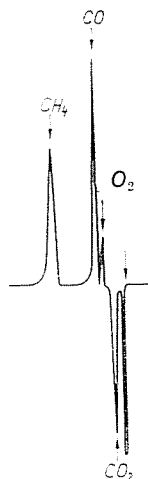

Fig. 2

gases by molecular sieves as described in the literature. Our system with activated charcoal wetted by glycerol is less sensitive in use and therefore it is more dependable.

Summary

A quick isothermic gaschromatographic method for the analysis of gas mixtures containing components of greatly different retention factors has been developed by utilizing both sides of a hot wire detector to detect the heavy, resp. the light components. The heavy components are eliminated from the gas stream by a specific trap after having been detected. The time of an analysis of a sample containing H_2, O_2, CO_2, CH_4 and CO is 3 minutes.

Literature

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