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CHROMATOGRAPHIC DETERMINATION OF CARBON MONOXIDE BELOW THE 1 ppm LEVEL

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SUMMARY

A chromatographic method is described for the determination of carbon monoxide at concentrations below 1 ppm. The setting of the instrument permits interfering components (oxygen, nitrogen and water) to be separated before the sample enters the chromatographic separation column. The conversion of carbon monoxide into methane is used for its detection with a flame ionization detector.

INTRODUCTION

Interest in the determination of carbon monoxide, the toxic properties of which have been known for a long time, has been increasing for several years. The main reasons for this renewed interest is connected with the increasing attention now being paid to environmental pollution¹⁻³, meteorological effects⁴ and technical problems arising from attempts to decrease the carbon monoxide contents of the atmosphere and technical gases^{5,6}. Studies are also being made of combustion processes in small appliances⁷, where human health can be affected, and of the effects of lengthy exposure to carbon monoxide on the content of carboxyhaemoglobin⁸. The formation of carbon monoxide in natural processes⁹ is also being investigated. The last three cases above, in particular, usually do not allow large volumes of gases to be taken for examination and therefore we have now developed a chromatographic method, which is sensitive enough even if small samples of gases are used.

A series of methods for the determination of carbon monoxide by chemical methods¹⁰ have been described in the literature and are today already considered to be classical. In most of these methods, carbon monoxide is oxidized to carbon dioxide by means of palladium dichloride or pentaiododioxide or by using an oxidative catalyst, and one of the reaction products (palladium, carbon dioxide or iodine) is then determined.

At present, more sensitive instrumental analytical methods¹¹ are used more frequently, in which carbon monoxide is determined colorimetrically¹², coulometrically¹³, conductometrically¹⁴, polarographically¹⁵ or chromatographically^{13,16-20}. Infrared spectrometry has also been used with success²¹. Most of the methods mentioned permit carbon monoxide to be determined down to concentrations of tens or units of

parts per million. Direct chromatographic methods reached a limiting sensitivity of several parts per million by means of reduction of carbon monoxide to methane¹⁸ and its subsequent detection with a flame ionization detector. A detailed study of the optimum hydrogenation conditions²² enabled concentrations of carbon monoxide down to 1–2 ppm to be determined. Chromatographic enrichment techniques²³ have not been used up to now, although they may be necessary in the future²⁴.

No proved method has been described that would permit the determination of tenths of a part per million, *i.e.*, $10^{-5}\%$ by volume, of carbon monoxide (the concentration of carbon monoxide in the atmosphere originating from natural sources) in samples of 20–50 ml. The method for the determination of carbon monoxide suggested here permits relatively large samples (20–50 ml) of gases to be introduced without substantially affecting the efficiency of the chromatographic separation, and provides the possibility for the separation of interfering components (oxygen and nitrogen) before the chromatographic column.

EXPERIMENTAL

The instrument consisted of two independent parts connected by a multi-way valve with a metallic pre-column (Fig. 1).

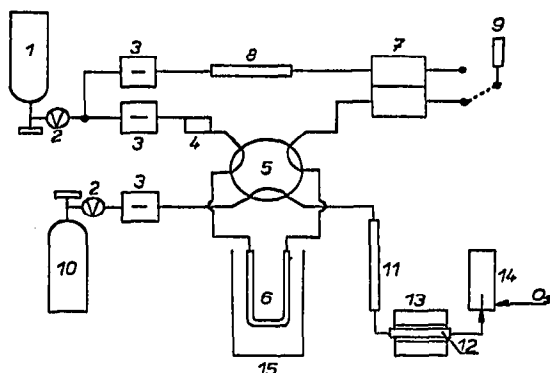


Fig. 1. Schematic diagram of the instrument. The components are identified in the text.

Hydrogen, used as the carrier gas in the first part of the instrument, was led from a pressure source (1) after having passed a pressure-reducing valve (2) and a second regulation step (3) into a sample injection port (4), from where it entered one arm of a six-way valve (5). A measuring cell of a katharometer (7) was connected to an outlet arm of the valve (5) in one of its positions. In the next position of the six-way valve, a U-shaped pre-column (6) made of copper tubing, 25 cm long and 4 mm in diameter, filled with molecular sieve 5A, was inserted into the path of the carrier gas. Hydrogen was taken in parallel from a T-piece behind the pressure-reducing valve (2) and led through the flow-rate regulator (3), which damped a column (8) filled with an inert support, and through a reference cell of the katharometer (7). A flow meter (9) was connected to the outlets of the cells.

A 3:1 mixture of hydrogen and nitrogen was used as the carrier gas in the sec-

ond part of the instrument. The gas was taken from a pressure cylinder (10) and, after reduction by means of the valve (2) and flow-rate adjustment by the regulator (3), it was led to another outlet of the six-way valve (5). A chromatographic column (11), 1.6 m long and 0.4 cm in diameter, filled with activated charcoal to a length of 25 cm and with Porapak Q in the remaining part, was connected to the valve outlet. A tube with a nickel-thorium catalyst (for its preparation, see refs. 18 and 22) (12), which was maintained at a constant temperature in an oven (13), was fixed to the column outlet. Gases produced in the tube with the catalyst were introduced into the flame ionization detector (14).

The katharometer signal was recorded on an EZ 4 recorder (Laboratory Equipment N.E., Prague, Czechoslovakia). The response of the flame ionization detector was led to a Vibron amplifier (EIL, Great Britain) and then recorded by a Servogor line recorder (Görtz, Vienna, Austria).

The sample was dosed into a stream of hydrogen and carried to the pre-column maintained at 0°. As soon as the katharometer indicated the appearance of a flow of oxygen and nitrogen, the six-way valve was switched into another position and the pre-column was heated to 80–90° (15). After being desorbed, carbon monoxide was separated from methane in the chromatographic column and, after being converted into methane, it was detected.

RESULTS AND DISCUSSION

The procedure for the determination of carbon monoxide used in this work is based on the utilization of increased sensitivity of chromatographic methods, which was achieved by decreasing the retention volume of the analyzed component and by using selective, highly sensitive detection. The elution of carbon monoxide in the dead volume was achieved by using a combination of activated charcoal and a porous polymer. Permanent gases (hydrogen, oxygen and nitrogen) obviously cannot be separated from the component being determined under these conditions. Therefore, a system for the selective detection of carbon monoxide based on its conversion into methane and on the use of a flame ionization detector was developed. In order to obtain the required sensitivity, the flame ionization detector must be operated under conditions close to those required for its maximum sensitivity. A constant flow-rate of nitrogen and hydrogen through the burner must be maintained and the entry of primary oxygen into the flame must be avoided. This requirement cannot be satisfied during direct injection of a mixture of oxygen, nitrogen and carbon monoxide at the moment when carbon monoxide passes through the detector, and therefore a combination of a column filled with molecular sieve 5A, in which the oxygen and nitrogen fraction is separated, was used. At lower temperatures (the dependence of retention volumes on temperature is shown in Fig. 2), nitrogen is sufficiently separated from the fraction of carbon monoxide to allow the transfer in the carrier gas path and the component under determination to be led into the separating columns filled with activated charcoal (where hydrogen is separated from carbon monoxide) and with Porapak Q (where carbon monoxide is separated from methane). The relative retention volumes of methane were not affected substantially by the use of activated charcoal (the retention time of methane is 1.51 on Porapak Q, compared with 1.49 on the column used, relative to the retention volumes of carbon monoxide), but the resolution of both components

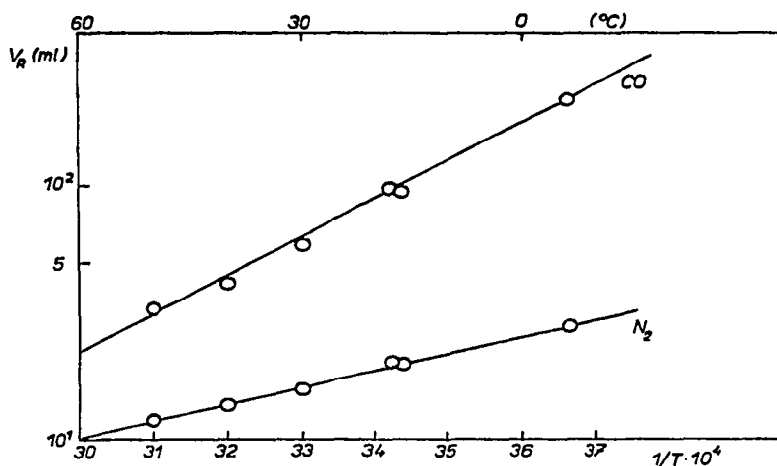


Fig. 2. Dependence of retention volumes (V_R) of nitrogen and carbon monoxide on the operating temperature.

was improved, which was unavoidable with regard to the possible access of methane in the samples under analysis. The use of the nitrogen-hydrogen mixture as the carrier gas has two results: it improves the operation of the flame ionization sensing element and it permits the catalytic hydrogenation of carbon monoxide to methane. Although the optimum ratio of flow-rates of nitrogen and hydrogen was 1.55, a ratio of 0.33 was used in our experiments as an increase in the ratio leads to a decrease in the efficiency of the hydrogenation catalyst and to lower reproducibility of the results. The use of nitrogen alone behind the hydrogenation catalyst was also unsatisfactory, as the flow-rates of the individual gases are disturbed by switching the flows of the carrier gases by the six-way valve. The noise of the base-line then substantially exceeds the fluctuations that arise when a mixture of nitrogen and hydrogen with a constant composition is used.

A mixture of nitrogen and carbon monoxide at a known concentration was used for the calibration of the instrument. The relative standard deviation, s_r , was 3.7% for seven experiments using the calibration mixture at a concentration of $2.5 \cdot 10^{-4}\%$ (v/v). The determination of carbon monoxide in selected samples of atmosphere (Table I) and expired air from persons working in the laboratory (Table II)

TABLE I
CARBON MONOXIDE CONCENTRATION IN SAMPLES OF SOIL AIR

Sample No.	CO content (ppm)
1	0.2
2	0.8
3	1.3
4	1.3
5	2.6
6	3.6

TABLE II

CARBON MONOXIDE CONCENTRATION IN SAMPLES OF EXPIRED AIR FROM PERSONS WORKING IN THE LABORATORY

Person	CO content (ppm)
D	0.7
K	0.8
T	0.8
H	2.8
W	3.3

were used as practical examples of analysis. The chromatograms were evaluated by measuring the area under the curves. With respect to the desorption temperature used, the retention time of carbon monoxide varied in the range 180–190 sec under otherwise constant conditions.

The system used for the introduction of the sample into a separation chromatographic column does not result in substantial peak broadening. While the width of the peak of carbon monoxide (expressed in terms of the time variance of the curve under the experimental conditions given), σ^2 , was 0.58 min on the column filled with molecular sieve 5A at 0°, the value measured after the chromatographic separation column decreased to 0.04 min. This is explained by the fact that the fraction of carbon monoxide passes most of the distance on the molecular sieve at the desorption temperature, *i.e.*, under the conditions when the variance is substantially smaller ($\sigma^2 = 0.02$ min at 50°). The introduction of the sample does not, therefore, lead to a decrease in the sensitivity of the methods as a result of peak broadening.

The injection syringe used for the introduction of sample into the column can be replaced with a sampling valve. It follows from Fig. 2 that the system used permits the use of substantially larger samples (*ca.* 150 ml) than those actually employed without any risk of the sample loss due to leakage from the column filled with molecular sieve. The connection used also permits the continuous control of the sorption efficiency of the column filled with molecular sieve by following the separation of oxygen from nitrogen as indicated by the response of the thermal conductivity detector. The sorption activity of the molecular sieve can vary to a considerable extent if samples that contain water vapour are analyzed, as the desorption temperature of carbon monoxide is substantially lower²⁰ than the temperature necessary for the desorption of water vapour from the surface of the molecular sieve.

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