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APPLICATION OF CHROMATOGRAPHY TO THE ANALYSIS OF EXHAUST GASES

M. KREJČÍ and K. TESAŘÍK

Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, Brno (Czechoslovakia)

SUMMARY

The arrangement of the chromatograph that is used for the determination of basic components in exhaust gases is described. An analysis for carbon monoxide, carbon dioxide, hydrogen, oxygen and total hydrocarbons takes 3 min. The error of the method was determined for individual components. The properties of the flame ionization detector when nitrogen and air are used for the introduction of the sample into the flame are compared.

In order to evaluate the change in the composition of the hydrocarbons in exhaust gases depending on the functioning of the engine, the enrichment technique was used for sampling. The method for sampling is described and the results obtained with different functioning of the engine of an Š 110 automobile are shown.

INTRODUCTION

The increasing pollution of the atmosphere has recently aroused interest in the exhaust gases from automobiles. At present, complicated and expensive analyzers are commercially available that can be used both for checking analyses according to specified tests and for technical studies. The main aim of these analyses is usually the determination of the contribution of vehicles to pollution, most often of the atmosphere, but often even the estimation of some fundamental technical parameters[1] is involved or more complicated technical conclusions[1,2] are drawn on the basis of such analyses.

The components of exhaust gases are divided into two categories, according to the technique used for sampling. The first category is represented by compounds that are sufficiently volatile to be sampled reliably in the gaseous phase and includes carbon dioxide, carbon monoxide, nitrogen oxide, nitrogen dioxide, volatile hydrocarbons, oxygen and hydrogen. The determination of the last two components is usually required for the calculation of mass or thermal balances of the engine operating in various regimes. Non-volatile compounds and the compounds contained in tar belong to the second category and samples of these compounds are taken exclusively through suitable filters after condensing non-volatile components (particularly water). Polynuclear aromatic hydrocarbons (PNAH), particularly those which have carcino-

genic properties[2,3], are then extracted from the tar and determined chromatographically.

When taking samples of the compounds of the first category, water is usually first condensed in coolers, as condensation was proved to affect neither the determination of permanent gases nor that of volatile hydrocarbons[4]. A single-stage sampling procedure was selected of three common techniques[5] when carbon dioxide, carbon monoxide, oxygen and hydrogen were determined. In order to determine the total non-volatile hydrocarbons, the proportional method for sampling was used.

Even if chromatography cannot replace continuously operating analyzers (mostly spectrophotometric analyzers, operating in the IR region, and sometimes chemiluminescence analyzers) as far as routine analyses are concerned, the chromatographic analyzer has several advantages. Firstly, as the components under investigation are determined in a single analysis and, consequently, the errors of individual analyzers are suppressed, the errors that arise are due to variations in the temperature of the individual cuvettes, delays in the transport of the gas being sampled and the time constant of the entire system. The small volumes of the sample necessary for the analysis (*ca.* 0.1 ml) represent a further advantage of chromatography. As a consequence, the sampling device, operating at a sufficiently high flow-rate of the gas being sampled, could be miniaturized and thus also the transport delay is small. The analyzer designed and described here is relatively cheap.

PRINCIPLE OF THE ANALYZER

Carbon dioxide, carbon monoxide, hydrogen and oxygen were analyzed in a single operation on the chromatograph used[6], which is shown in Fig. 1 and has two
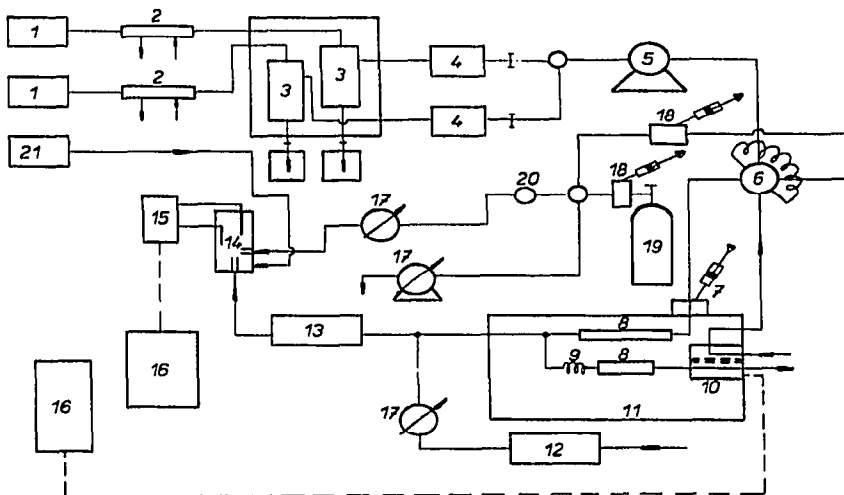

Fig. 1. Chromatographic analyzer for exhaust gases. 1 = Gas sampling; 2 = water condensers; 3 = coolers (5°); 4 = filters; 5 = pump; 6 = sampling valve; 7 = injection point; 8 = chromatographic column; 9 = pneumatic resistance; 10 = katharometer; 11 = thermostat; 12 = stabilizer of hydrogen flow-rate; 13 = hydrogenation catalyst; 14 = flame ionization detector; 15 = amplifier; 16 = recorder; 17 = flow meter; 18 = sampling device; 19 = calibration mixture; 20 = flow-rate regulator; 21 = air.

separating column systems connected in parallel. Nitrogen was used as the carrier gas. The total sample under analysis, introduced into the chromatograph by means of a six-way sampling valve, passes through the first chromatographic column. The column (18 cm long, I.D. 4 mm) is packed with the porous copolymer Synachrom (Lachema, Brno, Czechoslovakia). Carbon monoxide is eluted from this column in a single fraction together with any hydrogen or oxygen present. Selective detection with subsequent hydrogenation of carbon monoxide into methane is used for determining carbon monoxide. The methane thus produced is then detected with a flame ionization detector. Carbon dioxide is determined in the same way in the second fraction that leaves the first column. The stream of carrier gas is split into two portions after the first column. While one portion of the effluent from the first column is led into a hydrogenation catalyst and flame ionization detector, the other portion is led on to a column (15 cm long, I.D. 4 mm) packed with molecular sieve 5A. A thermal conductivity detector is connected after this column and its response, recorded on an independent recorder, represents the content of hydrogen or oxygen (the sensitivity for oxygen determination is not high with respect to the carrier gas used). The columns were placed in a thermostat at a temperature of 5°. The standard deviation for the determination of carbon monoxide (measured for a concentration of 1 %) was $\pm$ 3.4 % (relative), and for the determination of carbon dioxide (for a concentration of 10 %) was $\pm$ 1.5 % by volume (relative). The time of analysis was 90 sec.

The total content of hydrocarbons in exhaust gases was determined with a flame ionization detector of our own construction. The chromatographic system was arranged in such a way that a flame ionization detector connected after the hydrogenation catalyst could be used. Two basic arrangements for the introduction of the sample into the flame ionization detector were tested. The sample was introduced into the air supplied to the flame ionization detector according to the first arrangement. This arrangement enabled the sample of the gas to be led into the detector at a higher flow-rate so that the transport delay did not exceed 15 sec. The linearity of the response depending on the mass of hydrocarbons led in, however, did not exceed one order of magnitude of concentration[7]. The dependence of the response on the flow-rate of air through the detector passes through a maximum. This phenomenon is explained by the fact that the hydrocarbons, being led to the flame of the detector essentially by diffusion processes, have, from a certain air flow-rate upwards, been carried away from the flame before the ionization process in the burner could take place. Therefore, the second arrangement of the flame ionization detector was selected, in which the gas under analysis was led into the burner together with nitrogen. This arrangement provides linearity over several orders of magnitude of concentration. The transport delay increased to 45 sec on average.

The analyzer was used for studies on the influence of the ignition device of the internal combustion engine. An example of the results is shown in Fig. 2.

ANALYSIS OF THE HYDROCARBON PORTION OF EXHAUST GASES

During studies on the influence of incorrectly adjusted ignition on the exhaust gases from a combustion engine[8], the change in the composition of the hydrocarbons in the exhaust gases depending on an increase in the misfiring of the engine was investigated. The difference between the composition of the fuel being used and the com-
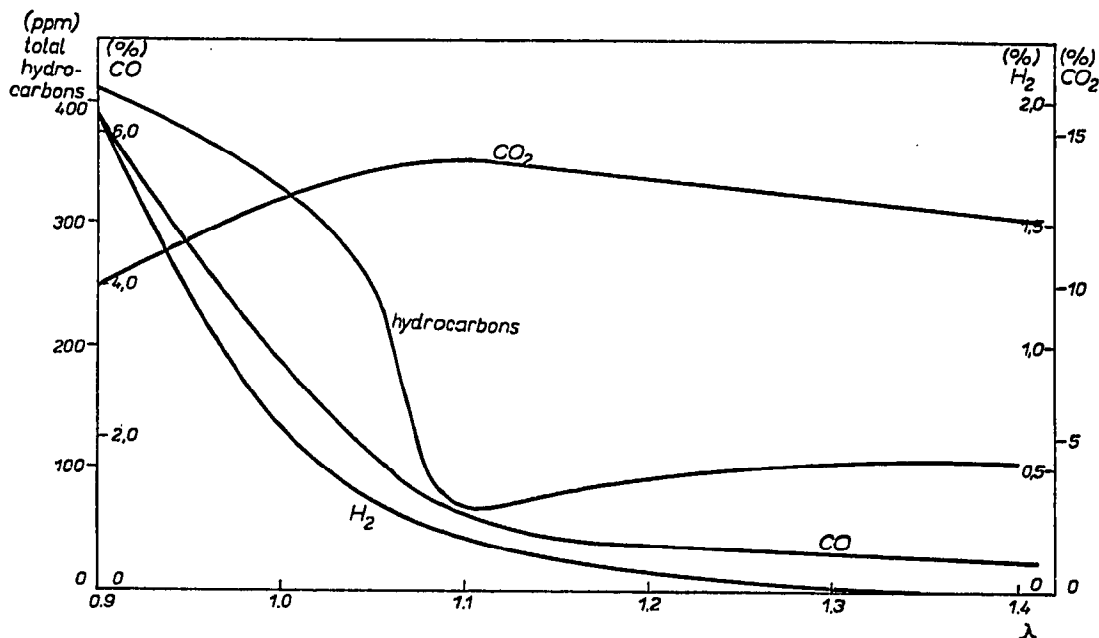
Fig. 2. Dependence of the concentration of the exhaust gases on the fuel–air ratio, λ.

position of the exhaust gases consists of a quantitative distribution of hydrocarbons according to their molecular weights. The hydrocarbons with low molecular weights, particularly methane[5], which is not present in the original fuel, are present in high proportions in the exhaust gases. Therefore, the adjustment of the composition of the samples under analysis was considered to be advantageous in the process of sampling and the principle of equilibrium absorption[9] was used. The gas under analysis was led through an absorption liquid (a paraffinic oil) which was enriched by the components being analyzed in the course of the sampling and, after completion of sampling, it was analyzed in a gas chromatograph. The partition coefficient, defined as the ratio of the components analyzed in the gaseous phase to the concentration of the component in the liquid phase, decreased as molecular weight of the hydrocarbons under analysis increased so that the absorption liquid, which was analyzed later, was enriched by the components with higher boiling points.

In sampling, 2 ml of absorption liquid were placed in a small bubbler and about 5 l of the exhaust gas were led into it, absorption taking place at 20°. Each sample was taken under an exactly defined stationary regime of the engine with a regulated and measured number of misfirings[8]. A 2-μl volume of the absorption liquid was taken for the chromatographic analysis in a Shimadzu GC 4A chromatograph. The column (5 m long, I.D. 4 mm) was packed with 10% (w/w) of Apiezon L on Chromosorb W. The analysis was carried out in an isothermal regime combined with temperature programming (60° for 10 min; 6°/min for 15 min; 150° for 25 min). After every three analyses, the column was heated to 300° and the components of the paraffinic oil were desorbed.

The chromatogram of the absorbate is shown in Fig. 3. In order to evaluate the difference, the original fuel was chromatographed under the same conditions, pre-
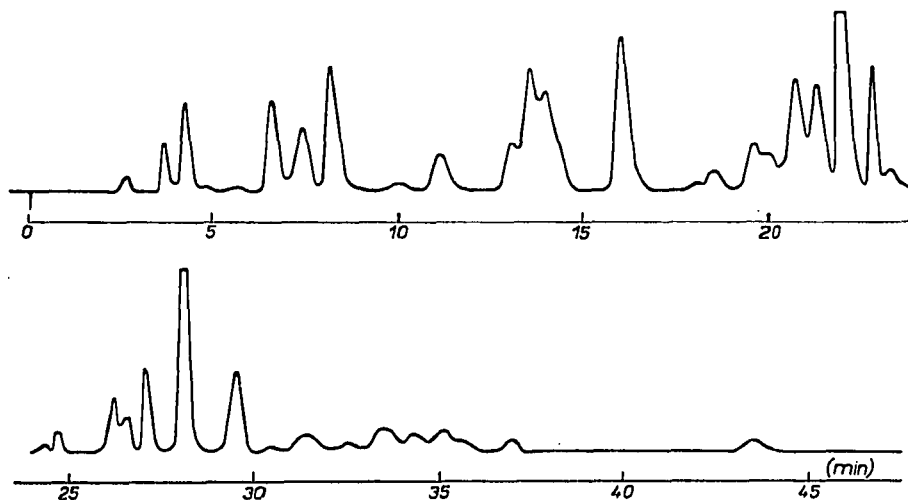
Fig. 3. Chromatogram of the hydrocarbons in the exhaust gas. The peaks are numbered from 2 to 38.

pared in such a way that 2 μl of "Speciál" petrol (N.E. Benzina, Czechoslovakia) were added to 2 ml of the paraffinic oil and 1 μl of the mixture thus prepared was injected into the chromatograph. As the quantitative determination of the difference between the composition of the original fuel and the composition of the hydrocarbons in exhaust gases was the only aim, the amount was evaluated by measuring the heights of individual peaks in the chromatogram. The change in the response of the flame ionization detector for individual types of hydrocarbons was neglected. Qualitative identification was not carried out.
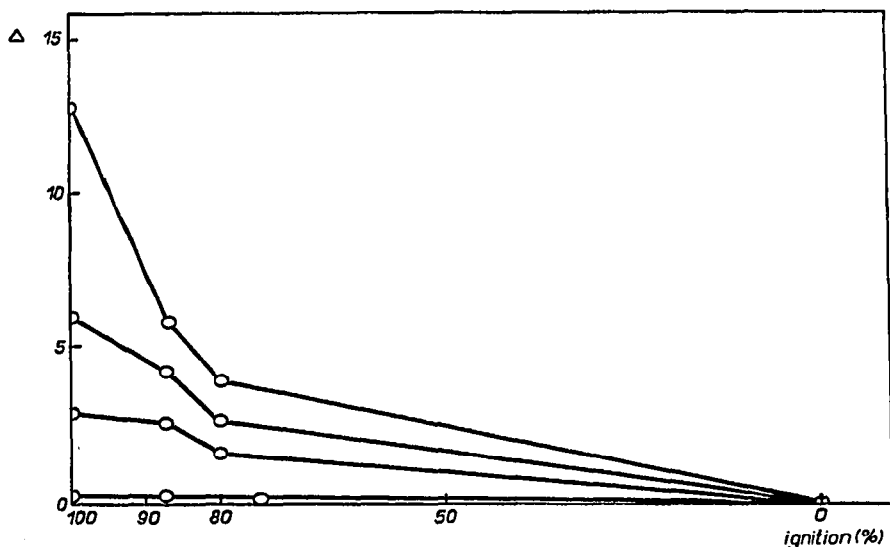

Fig. 4. Dependence of concentration differences of peaks Nos. 8, 10, 11, 22 (increasing series) on percentage of ignitions.

Individual peaks on the chromatogram were indicated by numbers from 2 to 38 together with the increase in the retention time. The heights of the peaks normalized in all instances to the height of peak No. 4, which equalled unity, were used for the quantitative comparison of the contents of individual peaks in the mixture under analysis. Normalized heights of the peaks in the chromatographic profile of "Speciál" petrol were taken as the basis and the heights of the fractions in the profiles of exhaust gases were subtracted from them. Selected results are shown in Fig. 4. Two extreme groups of fractions and a number of transition fractions were found in the chromatographic profiles. Fractions Nos. 8 and 22 can be considered to be the boundary cases. In the first case, the content of the component in the mixture does not change as a function of those cycles of the engine in which the ignition of the mixture did not occur. In the second extreme case (peak No. 22), the change is considerable.

The technique described can be used both for studies on the functioning of the engine and for studies on the effect of the composition of the fuel on the composition of the hydrocarbons in exhaust gases.

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