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Determination of carbon monoxide, methane and carbon dioxide in refinery hydrogen gases and air by gas chromatography

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Abstract

This paper illustrates a method for determining trace amounts of CO, CH_4 and CO_2 with the detection limit of 0.15, 0.15 and 0.20 μg/l, respectively, in refinery hydrogen gases or in air. A simple modification of a gas chromatograph equipped with a flame-ionization detector is presented. A Porapak Q column, additionally connected with a short molecular sieve 5A packed column and a catalytic hydrogenation reactor on the Ni catalyst have been applied. The principle of the analytical method proposed is the separation of CO from O_2 before the introduction of CO to the methanizer. The analytical procedure and examples of the results obtained have been presented. The modification applied makes it possible to use the GC instrument for other determinations, requiring utilization of the Porapak Q column and the flame-ionization detector. In such cases, the short molecular sieve 5A column and the methanizer can be by-passed.
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1. Introduction

Monitoring of trace amounts of gaseous impurities such as CO, CO_2 and CH_4 in refinery hydrogen gases is of great importance. It makes it possible to control various petroleum hydroconversion processes, e.g. catalytic hydrocracking or reforming, as well as processes of hydrogen manufacturing. For example, a few μg/l of CO present in the refinery hydrogen gases can cause irreversible loss of activity of the gasoline isomerization catalyst. Additionally, CO is highly toxic and its measurements at very low concentrations in indoor or workplace air are also very important [1].

Several analytical techniques for the determination of trace amounts of CO, CO_2 and CH_4 in refinery hydrogen gases and in air have been developed [2–15]. Commonly used indicator tubes allow for the determination of CO in air with the detection limit of 1.5 μg/l. However, the tubes are less sensitive towards CO_2 and CH_4. Interferents present in the sample, such as chlorinated organic compounds, hydrocarbons, alkenes in particular, affect the result of the determination. Therefore, activated carbon filters have to be applied in order to preclean the gaseous samples [2].

The use of electrochemical sensors for the determination of trace amounts of CO in the air

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requires removing from the sample chemical compounds such as H_2S, and SO_2 by using alkaline filters [3].

Fourier transform infrared spectroscopy has also been applied for simultaneous determination of trace amounts of CO, CO_2, CH_4 and other compounds in the air [4].

Gas chromatographic methods have been utilized for simultaneous determination of many compounds present in refinery hydrogen gases, air and any other gaseous mixtures [5–15]. However, quite expensive multicolumn refinery gas analyzers or similar multi-dimensional gas chromatographs equipped with thermal conductivity (TCD) and flame-ionization detection (FID) systems, without CO and CO_2 catalytic hydrogenation, are not sufficiently sensitive to determine trace amounts of CO and CO_2.

Test methods by gas chromatography and catalytic hydrogenation of CO and CO_2 require complex instruments [6–8]. Additionally, the use of the same gas chromatograph for other applications is usually impossible.

The aim of this study was to develop an analytical procedure for the determination of trace amounts of CO, CO_2, and CH_4 in refinery hydrogen gases or in air samples together with a suitable for this purpose, simple modification of a gas chromatograph equipped with a flame-ionization detector.

2. Experimental

2.1. Materials

Porapak Q, 120–180 μm (Waters, Milford, MA, USA); molecular sieve 5A, 120–150 μm (Serva, Heidelberg, Germany), activated at 350 °C for 6 h; nickel catalyst, 150 μm (Koch-Light, Colnbrook, UK), carrier gas: nitrogen (99.999% purity), FID gases: hydrogen (99.999% purity) and air (99.99% purity).

Standard mixtures containing CO, CO_2, and CH_4 in hydrogen were obtained using 8354 Gas Standards Generator (Matheson, Montgomeryville, PA, USA). Samples of refinery hydrogen gases and indoor air samples were collected at various points in the Gdañsk oil refinery plant (Rafineria Gdańska, Gdansk, Poland).

2.2. Instrument

A schematic diagram of a gas chromatograph modified for trace level determination of CO, CH_4 and CO_2 in refinery hydrogen gases, other process gases, or air, is shown in Fig. 1. A Carlo Erba, model HRGC 5300 gas chromatograph (Carlo Erba, Milan, Italy), equipped with a FID system, was used. The chromatograph was equipped with a split/splitless injector (1) (used in a splitless mode), a 3 m×3.3 mm I.D. stainless steel column packed with Porapak Q (2), a 3 cm×3.3 mm I.D. stainless steel column packed with molecular sieve 5A (5), a 4 cm×3.3 mm I.D. glass tube packed with Ni catalyst plugged with glass wool (6), a manual needle valve for controlling the hydrogen flow through the methanizer (Vici, Schenkon, Switzerland), two four-port UW type electromagnetic switching valves of 0.40 mm I.D. (Vici) (3,4) for by-passing the molecular sieve 5A column and/or the methanizer. A 0.5 mm I.D. stainless steel tubing was used throughout. The length of tubing used to connect any two units of the modified GC system did not exceed 10–15 cm.

2.3. Chromatographic conditions

Injector temperature was 80 °C. Samples, ranging in volume from 5 to 1000 μl, depending on the expected concentration of the analytes, were injected using a gas-tight syringe through a septum. The
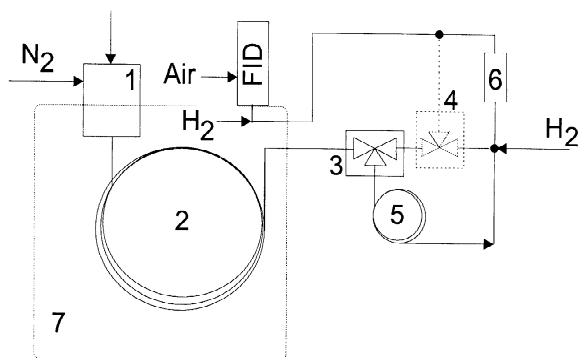

Fig. 1. Schematic diagram of a gas chromatograph modified for trace level determination of CO, CO_2 and CH_4 in refinery hydrogen gases and in air samples: 1, injector; 2, Porapak Q column; 3, 4, switching valves; 5, molecular sieve 5A column; 6, methanizer; and 7, oven.

column oven temperature was programmed. Initial 5 min isotherm at 30 °C was sufficient to complete the analysis. It was followed, if needed, by a 45 °C/min temperature gradient up to 190 °C and a second isothermal period of 25 min, permitting elution of hydrocarbons up to C7, which are present in some refinery hydrogen gases and can accumulate in the column. The detector and methanizer temperatures were 250 and 450 °C, respectively. The carrier gas (N_2) flow-rate was 30 ml/min. Hydrogen flow through the methanizer was 10 ml/min. FID gases (H_2 and air) flow-rates were 20 and 250 ml/min, respectively.

At first, for approximately 3.6 min the Porapak Q and molecular sieve 5A columns, as well as the methanizer, are connected in series. A gaseous sample (usually 500 μl) is introduced onto the Porapak Q column. After the elution of a CH_4 peak (3.3–3.6 min, depending on CH_4 concentration in an analyzed sample), the short molecular sieve 5A column is by-passed, in order to elute and determine CO_2 and hydrocarbons other than methane, present in refinery hydrogen gases. In the case of gaseous samples containing H_2S and/or mercaptanes, which can cause deactivation of the nickel catalyst, after the elution of CO_2, the methanizer is also by-passed using the additional three-way valve (dashed line in Fig. 1). The valve switching time for by-passing the molecular sieve 5A column was determined experimentally, based on the standard gaseous mixtures of CO, CH_4 and CO_2. The rule used was to elute methane completely, and to avoid introduction of CO_2 into the molecular sieve containing column.

3. Results and discussion

Examples of chromatograms of refinery hydrogen gases and warehouse indoor air, as well as the results of quantification of CO, CH_4, and CO_2, are shown in Figs. 2–4.

With the application of an efficient Porapak Q column, the order of elution of gas components is as follows: $CO/O_2/N_2/Ar$, H_2, CH_4, CO_2, C2, C3, etc. [16].

Under the experimental conditions mentioned above, the obtained peak resolution is sufficient for
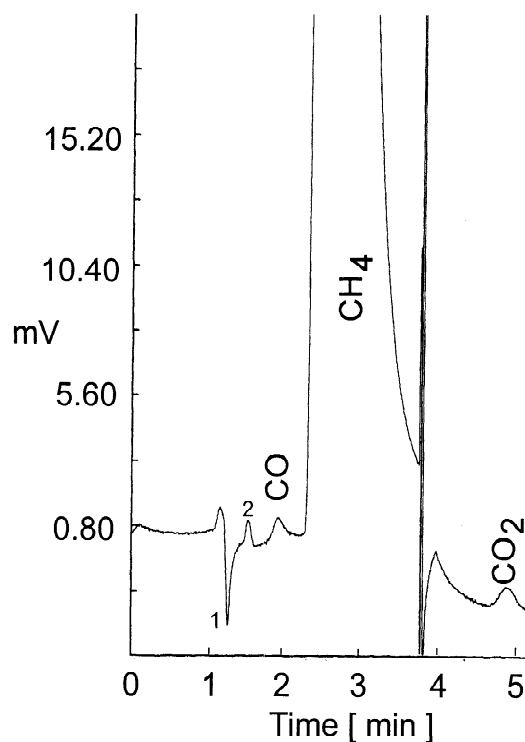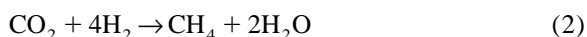

Fig. 2. The chromatogram of hydrogen gas supplying the isomerization reactor: CO 2.1 μg/l; CH_4 >9 mg/1 (out of scale); CO_2 0.9 μg/l; 1, hydrogen dip; 2, oxygen caused peak. Chromatographic conditions as described in the Experimental section.

quantitative determination of CO, CH_4, CO_2 and many other components of a gaseous sample detectable by FID, with or without CO/CO_2 catalytic hydrogenation. However, CO is co-eluted with O_2, which is commonly present at low concentrations in imperfectly collected samples of different hydrogen refinery gases and at high concentrations as a component of air samples. In consequence, determination of trace amounts of CO with the only use of Porapak Q column and catalytic hydrogenation–FID system may bear an unpredictable error, caused by the undesired chemical reactions (3) and (4), occurring on the surface of the nickel catalyst.

The main chemical reactions on the surface of the Ni-catalyst are as follows [17]:
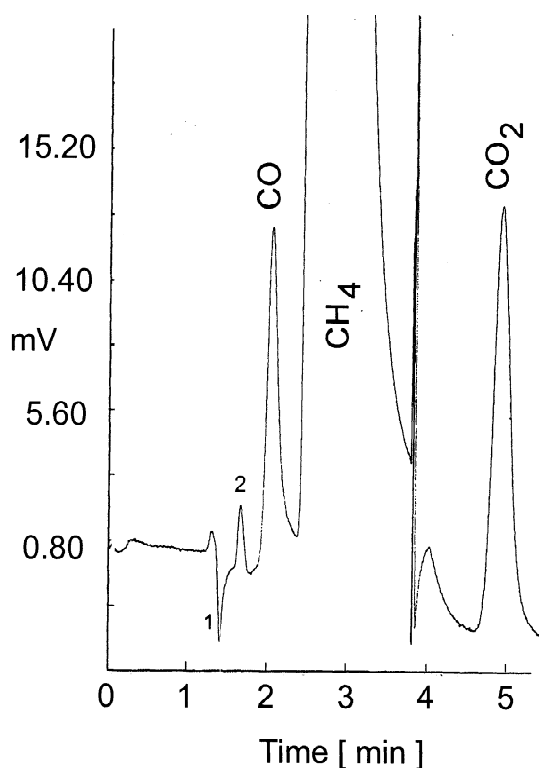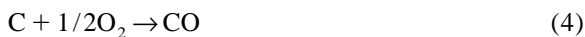
$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{1}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{2}$$

Fig. 3. The chromatogram of hydrogen gas feeding the hydrogen recovery plant: CO 32.2 μg/l; CH_4 >9 mg/l (out of scale); CO_2 19.6 μg/l; 1, hydrogen dip; 2, oxygen caused peak. Chromatographic conditions as described in the Experimental section.

Fig. 4. The chromatogram of the warehouse indoor air, where lift-trucks powered with propane–butane engines are in use. CO 19.5 μg/l; CH_4 1.3 μg/l; CO_2 142 μg/l; 2, oxygen caused peak. Chromatographic conditions as described in the experimental section.

Additionally, the following reactions can occur, contributing to the inaccuracy of the results [17]:

$$CO_2 + C \rightarrow 2CO \tag{3}$$

$$C + 1/2O_2 \rightarrow CO \tag{4}$$

In practice, trace amounts of carbon are deposited on the surface of the nickel catalyst, probably originating from the hydrocarbons present in refinery hydrogen gases or from gaseous samples containing large amounts of CO_2. This carbon, in the presence of oxygen or carbon dioxide, can be converted to carbon monoxide, causing an increased FID signal for CO (if its peak is not resolved from oxygen) and CO_2 (due to reactions (3) and (4), and subsequent hydrogenation).

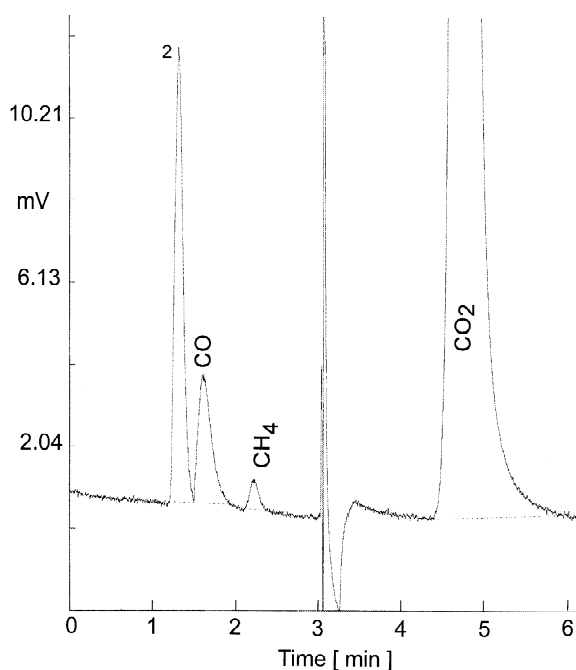The interferences described above are of particular importance and must be taken into account, when the traces of CO have to be determined. On the other hand, the experimental results obtained by the authors indicate that the multiple injections of air in order to oxidize trace amounts of carbon on the hydrogenation catalyst, recommended in Ref. [8], are not sufficient. Their effect is rather short lasting and is quickly followed by repeated carbon buildup on nickel, particularly when the analyzed gaseous samples contain CO_2 and/or hydrocarbons.

Peaks corresponding with O_2 elution, result from reaction (4) in connection with reaction (1). The illustration of this phenomenon is shown in Fig. 5. The area of peaks caused by oxygen varies, depending on carbon content on Ni catalyst surface and, to a lesser extent, on the amount of oxygen in the analyzed gaseous sample.

In the presented method, the influence of this unfavorable effect on the accuracy of the results of the CO determination has been eliminated by using a short column packed with molecular sieve 5A, which
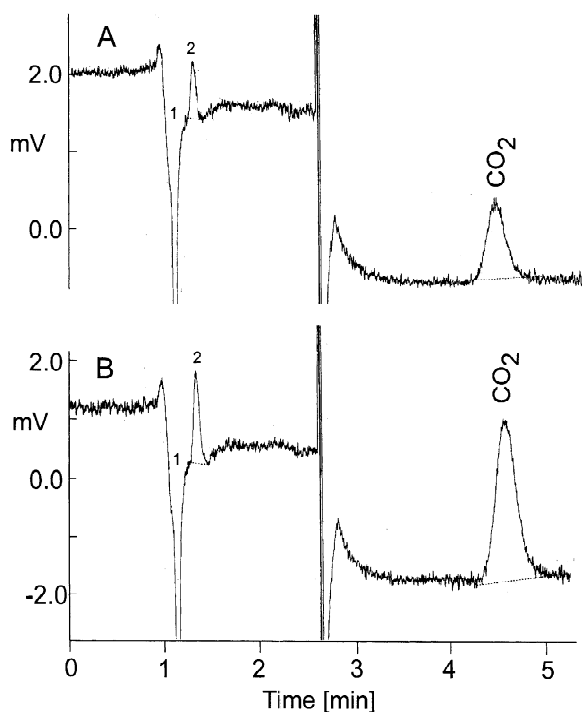
Fig. 5. The chromatograms of hydrogen of 99.9999% purity spiked with outdoor air. (A) Dosed sample contained 0.13 mg/l of oxygen. (B) Dosed sample contained 0.65 mg/l of oxygen. 1, hydrogen dip; and 2, oxygen caused peak. Chromatographic conditions as described in the Experimental section.

is frequently connected in series with Porapak Q column, in order to separate CO from O_2.

The length of this short molecular sieve 5A column has to be chosen in such a way as to permit CO elution between the peaks of oxygen and methane. The application of too long a molecular sieve 5A column will cause overlapping of CO and CH_4 peaks or even elution of CO after CH_4. On the other hand, the overlapping of the CO peak with peak caused by oxygen is a result of the application of too short a 5A molecular sieve column or of unsatisfactory activation of the 5A adsorbent.

After the elution of CH_4 (approximately 3.3 to 3.6 min), a short column packed with molecular sieve 5A must be by-passed using a manual or an automatic switching valve. Subsequently, CO_2 is eluted and determined after hydrogenation. The concentration of other hydrocarbons, such as C_2, C_3, etc. up to C_7, can be also determined, if needed.

The by-passing of a molecular sieve 5A column is necessary in order to avoid polluting it with CO_2, which is irreversibly adsorbed onto this adsorbent at temperature of 30 °C and, under such circumstances, cannot be determined. Moreover, the by-passing of a 5A column may also help to avoid molecular sieve deactivation due to the presence of water, H_2S, hydrocarbons higher than C_4, and/or other polar components potentially found in various analyzed samples. It is also very important to utilize dried carrier gas (N_2, Ar or He) [14].

The baseline dip (at 1.2 min), visible on the chromatograms (Figs. 2, 3, 5 and 6), corresponds to hydrogen elution. This is caused by a momentary introduction of an additional amount of hydrogen to the burner (500–1000 μl, depending of the volume of the dosed sample). This was checked experimentally by dosing hydrogen of 99.9999% purity.
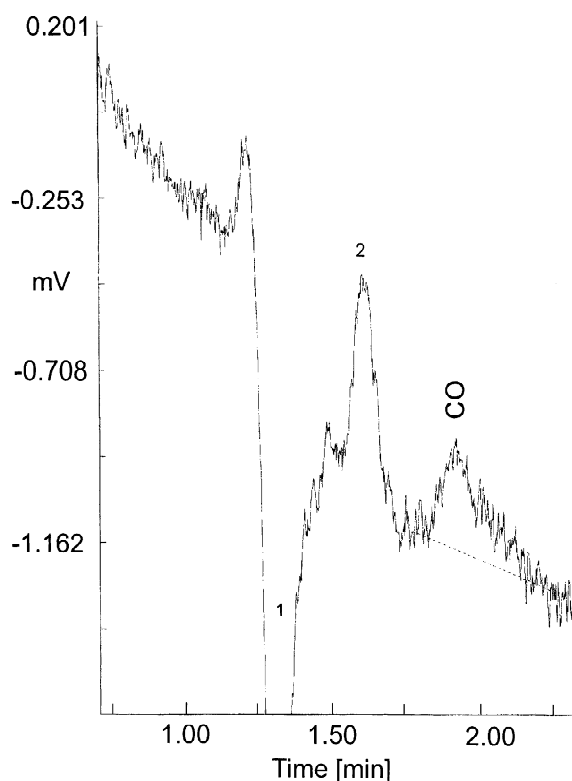

Fig. 6. Enlarged fragment of the chromatogram obtained for a 1.0 ml sample of refinery hydrogen gas. CO 0.2 μg/l; 1, hydrogen dip; 2, oxygen caused peak. Chromatographic conditions as described in the Experimental section.

The technical solution of the gas chromatograph, presented in Fig. 1, and the simple analytical method proposed, permitted avoiding overestimation of the CO contents in the gaseous samples due to reaction (4). The developed modification of the gas chromatograph has not solved, however, the problem of overestimation of trace amounts of CO_2 in analyzed refinery gases (reaction (3)). For this reason, the obtained coefficient of the calibration curve for CO_2 is higher than those for CO and CH_4 (the last two are equal). The extent of overestimation depends on the amount of carbon buildup on the surface of the nickel catalyst. The instability of the coefficient of the calibration curve observed for CO_2 can be easily eliminated by frequent recalibration of the system. In our laboratory recalibration of the chromatographic system is usually performed every 200 samples.

The calibration of the method was performed with gas standards of $CO/CO_2/CH_4$ in hydrogen. The statistical data for the calibration curves are collected in Table 1. For five point calibration curves for CO, CO_2, and CH_4, the values of the coefficient of determination, R^2, better than 0.999 have been obtained. The FID response is linear over five orders of magnitude. The detection limits based on the signal-to-noise ratio (S/N) of 3 for a 1000 μl sample have been determined. The corresponding chromatogram of trace amounts of CO is shown in Fig. 6. For seven independent determinations of CO content at 1.5 μg/l level, CH_4, and CO_2 (both at 2.0 μg/l level) in a 500 μl gaseous sample, the values of relative standard deviation (RSD) were found to be 3.9, 1.0, and 4.1%, respectively.

The described method of determination of CO, CH_4, CO_2 at trace concentration level in the refinery hydrogen gases and in the workplace air, as well as the GC instrument presented have been in use for over 2 years in our laboratory (approximately five analyses/day). The same GC is used for other purposes with the 5A column and the methanizer is by-passed.

When the concentration of the determined gaseous components exceeds the calibration range, the injected sample volume should be lower then 500 μl. In this case, the concentration of each component can be calculated on the basis of the ratio of the sample volume injected during calibration to the sample volume of the presently injected sample.

A short molecular sieve 5A column, after activation, can be used for more then 1 year when dried carrier gas is utilized, unless CO_2, H_2O, H_2S and SO_2 are permitted to enter it. Worsening resolution of CO and oxygen caused peaks is a sign of the deactivation of the molecular sieve. In consequence, the adsorbent must be re-activated as described in the Experimental section.

4. Conclusions

A simple gas chromatographic method has been presented, which utilizes a flame-ionization detector for the accurate and precise determination of trace amounts of CO, CO_2 and CH_4 in the refinery hydrogen gases, in the indoor air, and in other process gases.

The method and instrument modification described make it possible to determine trace amounts of CO, CO_2 and CH_4 (with no other hydrocarbons present in the sample) within 5 min. The level of detection for a 1000 μl gaseous sample has been evaluated for CO, CO_2, and CH_4 as 0.15, 0.15 and 0.20 μg/l, respectively.

The possibility of using a Porapak Q packed column and a flame-ionization detector for other chromatographic analyses, without the necessity of

Table 1
Statistical data for calibration curves

Compound	Calibration range (μg/l)	R^2	Detection limit (μg/l) ($S/N = 3$)
Carbon monoxide	0.3–3750	>0.999	0.15
Methane	0.3–1900	>0.999	0.15
Carbon dioxide	0.4–1400	>0.999	0.20

disconnecting the modified part of the system, is an additional advantage of this method.

The disadvantage of this method is the necessity of frequent recalibration, in order to avoid the erroneous determination of very low CO_2 concentrations.

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