

DETERMINATION OF N-BUTANOL AND ISOBUTANOL IN GASOLINE USING GAS CHROMATOGRAPHY (GC-FID)

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Abstract. The paper is focused on the identification of laboratory quantities of n-butanol and isobutanol by gas chromatography GC-FID. Gas chromatography (GC) is a type of separation method. It is based on separation of components contained in the test sample that can be converted into the gas phase without decomposition. The process of separation of substances takes place in the gas chromatograph column. The mobile phase is always a gas which is in contact with the stationary phase. This assessment is also based on the application of n-butanol and isobutanol as high-percentage blends for possible future use. For laboratory analysis various combinations of fuels were collected containing gasoline with always one of the alcohols or with both together. The result is a chromatographic record, which is characteristic for each petroleum fraction. Using the chromatogram can clearly identify the presence of alcohol, which is necessary to ensure and check the prescribed amount of alcohol in the fuel. Gas chromatography can thus supplement the results of the evaluation of standard fuel or narrow selection of test parameters. The proposed method is an alternative to commonly used multidimensional chromatography.

Keywords: n-butanol, isobutanol, GC-FID, gasoline, retention time.

Introduction

Recent fuels for any engine are complex blends of fuel ingredients. Some parts of blend are a product of crude oil distillation. Other products are produced by hydrocracking, catalytic cracking and by pyrolysis of vacuum distillates and heavy residues of distillation. Paraffins, olefins and aromates from crude oil compose resulting in fuel. Further, non-crude oil additives are composed of oxygen matters and methylesters in fuels. Therefore, it is not possible to examine fuel without examination of its parts. Also for the blending procedure and development of new fuel products an assessment of quality of properties and quantity of fuel parts is needed [1].

Traditionally, gas chromatography (CG) of gasoline is used for assessment of groups of hydrocarbons and additives, which are composed of oxygen substances. Multidimensional chromatography is the most precise method recently. Assessment of liquid petroleum products for automotive-motors is done according to the standard EN ISO 14517.

Generally, chromatography is a physical-chemical method dividing liquid and gaseous blends according to different affinity of parts of blend towards mobile and stationary phases [2]. During the separation process molecules are repeatedly transported to the stationary phase and back to the mobile phase [3].

The mobile phase penetrates the stationary phase of blend separating its parts. This washing out is the principle of chromatography. Released parts of blend are transported in the direction of streaming mobile phase. The period until the stationary phase is keeping molecule of substance on its surface is proportionate with the strength of interaction between the substance and the stationary phase. Substances released from the stationary phase are measured on column output. Generally, the stronger interaction the later release of the substance from the stationary phase [4].

Gasoline sample is injected into automatically managed system of six chromatographic columns. Depending on number of carbon atoms in molecule of each group of specific hydrocarbons separation occurs being detected by a flame-ionisation detector (FID). Groups of n-alkanes, cycloalkanes, olefins, cycloolefins, aromatics and oxydated substances having from 3 to 10 carbon atoms are separated from gasoline at the end. Hydrocarbons with number of atoms above 10 are separated as saturated aromatic hydrocarbons [5].

Bioethanol (or as E85) is commonly and commercially used as gasoline additive. Use of biobutanol is not scheduled yet, although it has characteristics and especially because it is not hygroscopic. Biobutanol is preferable for replacement of bioethanol. Biobutanol can exist in the form of n-butanol, and also in the form of isobutanol. This paper works with the variant of adding isobutanol to its determination in gasolines and in blends with n-butanol. In the event of putting biobutanol to the fuel market it will also be needed to monitor compliance with the statutory limits.

Materials and methods

A simple analytical method for determination of isobutanol and n-butanol in gasoline and diesel fuel using GC-FID was developed and verified. A sample of pure gasoline containing 32.21 % vol. of aromatic hydrocarbons, 10.29 % vol. of olefins, and 0.52 % vol. of benzene was analysed according to the standard EN 228 for the winter season (class F1). The water content was 48.00 mg.kg⁻¹ and oxidation stability exceeded 360.0 minutes. The tested n-butanol and isobutanol were in p. a. quality (LachNer Ltd., CZ); isooctane used as the sample solvent also in p. a. quality (Lachema Brno, CZ). Guaranteed Reagent is the ideal quality for laboratory purposes. Batch to batch reproducibility is specially controlled to guarantee consistent analytical results. The grade is equivalent to Analytical grade (A.R.) Reagent grade (R.G.) or p.a. nomenclature of other manufacturers. Nonane puriss (certified by Slovak Institute of Metrology, Bratislava) was used as the internal standard.

Test samples with the following composition (all figures in % vol.) were prepared:

1. n-butanol in gasoline: 10 %, 30 %;
2. isobutanol and n-butanol in gasoline: 5 % and 10 % (each component).

These samples of gasoline were stored in dark brown glass bottles (with the volume of 20 ml). The volume percentages were calculated according to the volumes of individual components before blending.

Prior to the GC analysis, all samples of gasoline were diluted according to the following scheme: 1000 µl of isooctane + 10 µl of gasoline + 10 µl of nonane (dilution with a suitable solvent, in this case isooctane, enables better resolution of individual components during the separation process). The gas chromatograph equipped with a fused silica capillary column and a flame ionization detector was used for the measurement. The instrument parameters and measurement conditions are shown in Table 1.

Table 1

Parameters of gas chromatograph with FID detector

Chromatograph	Varian 3300
Analytical column	DB-5, 30 m x 0.25 mm i.d., film thickness 0.25 µm
Injection technique	manual at 280 °C, sample volume 1 µl, split ratio 1:20
Carrier gas	nitrogen 1 ml.min ⁻¹
Temperature program	50 °C (3 min), gradient 8 °C.min ⁻¹ , 260 °C (5 min)
FID detector	280 °C, hydrogen 30 ml.min ⁻¹ , air 300 ml.min ⁻¹
Software for data collection	Star Chromatography Workstation vs. 4.51

The quantities of individual substances (isobutanol, n-butanol) were calculated according to the following formula (1):

$$c_i = \frac{P_i}{P_s} \cdot c_s \cdot k_i \quad (1)$$

where c_s – concentration of internal standard;
 c_i – concentration of analysed component (n-butanol or isobutanol);
 P_i – area of respective peak;
 P_s – peak area of internal standard (nonane);
 k_i – coefficient calculated from the respective calibration curve.

The calibration curves for n-butanol and isobutanol were measured using standard solutions at three concentration levels (1000 µl of isooctane + 2 µl or 5 µl or 10 µl of alcohol + 10 µl of nonane; with two repeated injections at each concentration level). All calculations were performed automatically using the chromatographic software, which is also specified in Table 1.

Results and discussion

Figures 1-4 are chromatograms of fuel where R is detector response in volts and t_R is retention time in minutes.

Table 2 shows the measured values of the alcohol concentrations in gasoline evaluated by the GC-FID method. All values were calculated as the arithmetic mean from three GC measurements.

Table 2

Measured concentrations of n-butanol and isobutanol in gasoline

Fuel	The measured concentration of alcohol (% vol.)
Gasoline + n-butanol 10 % vol.	8.94
Gasoline + n-butanol 30 % vol.	33.88
Gasoline + n-butanol 5 % vol.+ isobutanol 5 % vol.	5.90 + 7.72
Gasoline + n-butanol 10 % vol. + isobutanol 10 % vol.	11.06 + 11.99

Numbers above the peaks of the chromatogram are values of retention time of the measured substances in minutes. Retention times of the measured substances are compared with the retention time of standards for n-butanol and isobutanol. Quantity is identified from the area below the peaks as described above.

Figure 1 shows that butanol can be blend with European gasoline up till 10 % vol. according to the maximal allowed content of oxygen substances and the standard EN 228. US gasoline can absorb 11.5 % vol. of n-butanol (or isobutanol). It is expected that 16 % vol. of butanol to gasoline will be blend, which is allowed without modification of the engine.

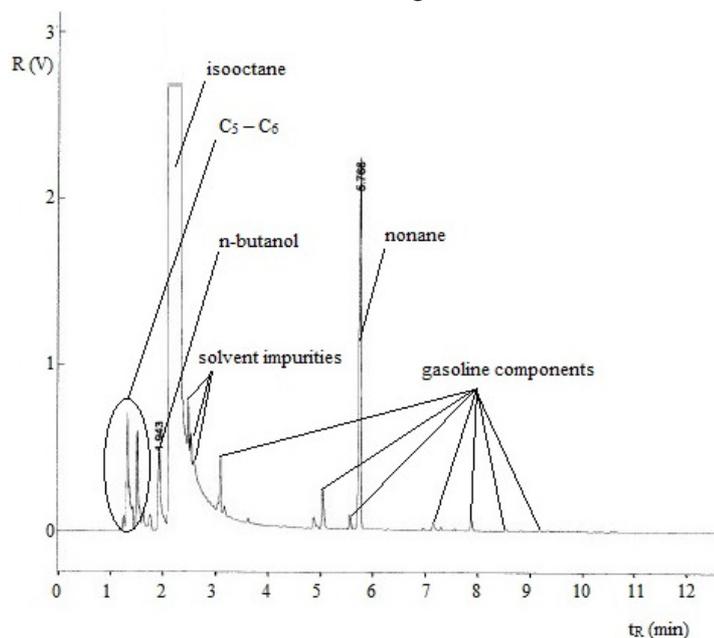


Fig. 1. Gasoline with 10 % vol. of n-butanol

For fuel blends with a high proportion of biobutanol a low proportion of gasoline is necessary, less extensive technical modifications of original gasoline fuel system vehicles than in the case of blends with a high content of bioethanol. 30 % vol. of n-butanol (Figure 2) in gasoline would not have more significant influence on the fuel gasoline parameters. With such amount it is already, however, needed to watch the vapor pressure of the fuel blend, which will be lower than of pure gasoline and could cause starting problems at low temperatures.

It is important to know the area below the peak of the measured substance and one of internal standard nonane to calculate the concentrations of n-butanol and isobutanol in gasoline in our case. The four displayed figures with different percentage of alcohol show each the measured substance well separated. The measured value of each sample has approximately 10 % difference opposed to the parts of the sample (Table 2). But, it was not intended to evaluate precision of the method. Improved

precision of the measured quantitative values is expected if a new chromatograph with auto-sampler and electronic regulation of the gas stream is used.

Conditions of chromatographic separation were found as both n-butanol and isobutanol are well separated from other parts of the sample, especially from C₅ and C₆ fractions.

A highly effective, but expensive method of multidimensional chromatography is recently used for assessment of substances like n-butanol or isobutanol. Unfortunately, only well-equipped organisations may afford to buy such equipment. Therefore, development of a cheap and simple method for assessment of the parts of fuel blends was the objective of this article according to the standard EN 14517 using the multidimensional gas chromatography method [1; 2; 6].

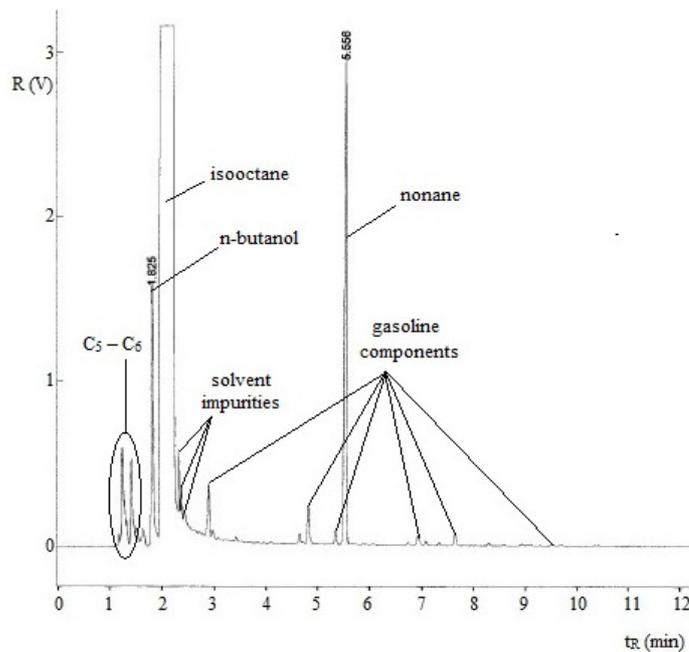


Fig. 2. Gasoline with 30 % vol. of n-butanol

Alcohols n-butanol and isobutanol have small differences between the parameters. The resulting impact on the parameters of gasoline with 5 % vol. of n-butanol + 5 % vol. of isobutanol should correspond approximately to influence of 10 % vol. of n-butanol or 10 % vol. of isobutanol, Figure 3.

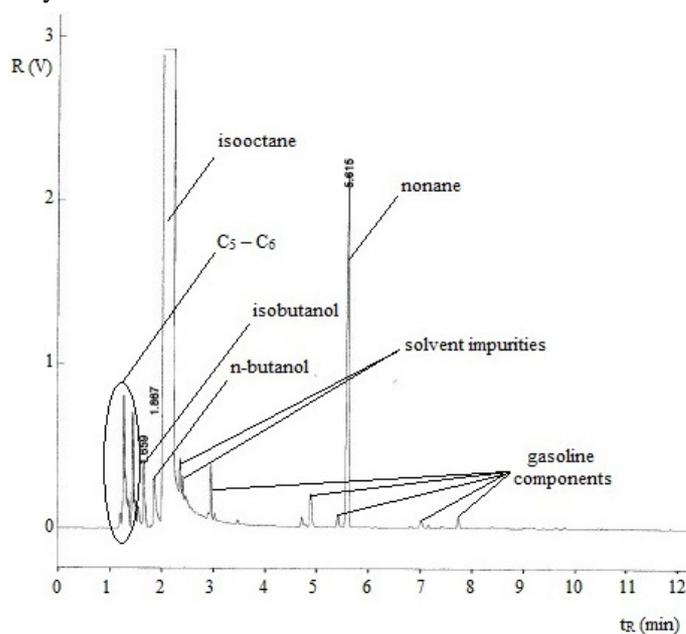


Fig. 3. Gasoline with 5 % vol. of n-butanol and 5 % vol. of isobutanol

Gasoline engines can burn blends of gasoline with biobutanol created in any ratio of components (Figure 4), but the blend may also be used alone (100 %) as a propulsion fuel in internal combustion engines. This is because its characteristic is closer to gasoline than to bioethanol.

The method of gas chromatography has assessed both n-butanol and isobutanol (Fig 3 – 4) while the peaks of C₅, C₆ fractions and mobile phase (isooctane) were separated. Also internal standard must be selected properly to be seen in sufficient distance from the analyzed substances at the chromatogram. The selected internal standard nonane has fulfilled this condition well.

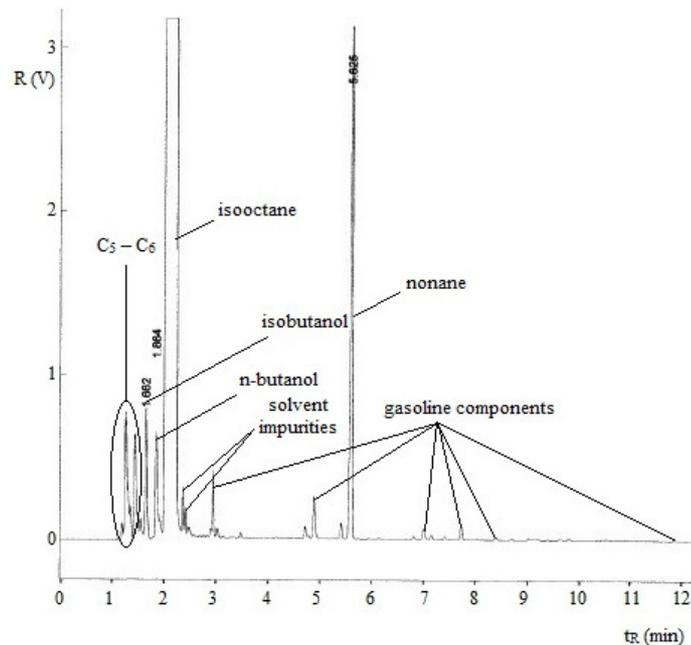


Fig. 4. Gasoline with 10 % vol. of n-butanol and 10% vol. of isobutanol

Minimal differences between the retention times of the analyzed substances in Figures 1 – 4 show very good reproducibility of the retention time. The higher the peak with a larger area, the higher the concentration of the measured substance.

Interval 0-12 minutes was selected because the assessed substances occur in it. Other components of gasoline, which are out of this interval, were not substantial for assessment of n-butanol and isobutanol. The peak of unmeasured solvent isooctane was cut off in order to improve the explanatory power of Figures 1-4.

Conclusions

The described methods of gas chromatography are used in the control of fuel according to the requirement standards. In the analysis of motor fuels gas chromatography (GC) is used mainly in monitoring the quality of automotive gasoline and liquefied petroleum gas (LPG). For the determination of oxygenates and the total oxygen content of automotive gasoline the method of gas chromatography is also prescribed. Besides this method, which is prescribed by the quality requirements according to DIN EN ISO 228, other alternative standardized procedures (EN, ASTM, DIN, ISO) can be also used that are using gas chromatography to analyze automotive gasoline. As an example there could be determination of the content of benzene, aromatic hydrocarbons or the group composition of the gasolines.

Multidimensional chromatography is recently used for assessment of bioethanol and ethers according to the standard EN 14517. The method is very cost-intensive. According to the results of the article the GC-FID method may be used. The internal standard must be selected properly to be seen in sufficient distance from the analyzed substances at the chromatogram.

For determining of n-butanol and isobutanol the interval of 0-12 minutes is enough, because the assessed substances occur in it. The C₅ and C₆ fractions can also be readily identified. Other

components of gasoline, which are out of this interval, were not substantial for the assessment of n-butanol and isobutanol.

In addition, GC-FID can supply the results of standard assessment of fuel or vice versa streamline and narrow selection of evaluation parameters.

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