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INNOVATIVE TECHNOLOGIES IN THE OIL AND GAS INDUSTRY

ANALYSIS OF COMPONENTS OF ROCKET KEROSENE BY COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY/TIME-OF-FLIGHT MASS SPECTROMETRY

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The components of rocket kerosene were determined by comprehensive two-dimensional gas chromatography/time-of-flight mass spectrometry (GCЧGC/TOFMS) under pre-defined analytical conditions. Qualitative analysis was performed by identification of the various groups of the compound on a structured chromatogram. Quantitative analysis was performed by estimating the areas of the respective characteristic peaks. It was found that the kerosene contained paraffins, monocyclic, bicyclic, and tricyclic alkanes, alkenes, and aromatic and oxygen-containing compounds. It was demonstrated that GCЧGC/TOFMS has obvious advantages over traditional methods for determining the components of rocket kerosene.
Keywords: *comprehensive two-dimensional gas chromatography, time-of-flight mass spectrometry, rocket kerosene*

Comprehensive two-dimensional gas chromatography (GCЧGC) is a comprehensive method of chromatographic analysis developed in the 1990s [1]. It is based on the use of two chromatographic columns that separate the substances independently of each other by various mechanisms (e.g., columns with polar, nonpolar, or chiral stationary phases) linked to each other by a modulator. Because the substances in the mixture have similar boiling points they cannot be separated completely in the first column (^{1}D); for this they

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are directed in pulses to the second column (^{2}D) through the modulator. Unlike traditional unidimensional gas chromatography comprehensive two-dimensional chromatography has high resolving power and sensitivity, higher peak capacity, and shorter duration and makes it possible to obtain more information.

Since the nineties, time-of-flight mass spectrometry (TOFMS) has become one of the widely used methods of spectral analysis. It is based on the principle that in a constant electric field ions with identical kinetic energy and different charge/mass ratio have different times of flight from source to detector. This makes it possible to estimate the composition or the structure of the material being investigated. The method also has advantages such as high sensitivity and efficiency and also makes it possible to conduct an analysis without any limitations with regard to the mass of the investigated sample. The CG–CG and TOFMS methods can be used together for qualitative and quantitative analysis of samples with complex compositions. At the present time the methods have given satisfactory results in the analysis of samples in the perfumery and petrochemical industries and in medicine [3-8].

Rocket kerosene is the main fuel used in a new type of high-thrust carrier rocket and may in the future become the most widely used rocket fuel in China. However, its properties and performance are largely determined by its composition, and for this reason determination of the composition of rocket kerosene is essential for improving its production technology, processing, quality control, and application [9, 10]. The aim of the present work was therefore to analyze the composition of rocket kerosene by GC-GC and TOFMS.

The CG-GC/TOFMS analyzer consisted of an Agilent chromatographic system (USA) with an automatic Agilent 7683 injector and a ZX-2 modulator and a "FasTof" time of flight mass spectrometer (ZOEX, USA). The NIST08.L database of mass-spectral data was used to interpret the spectra.

For total analysis by two-dimensional gas chromatography a column with a weakly polar stationary phase can be used as ^{1}D column, and a column with a polar stationary phase can be used as ^{2}D column. In the present investigation the ^{1}D column (DB-5) was a capillary column 15 m in length and 250 μm in internal diameter with a weakly polar stationary phase, and the thickness of the layer of stationary phase was 1 μm. The ^{2}D column (BPX-50) had a length of 1 m and an internal diameter of 100 μm, and thickness of the film of stationary phase was 0.1 μm. The carrier gas was helium with a volume flow rate of 1 ml/min. The kerosene sample (0.2 ml) was introduced into the system by the split-flow technique. The temperature of the inlet and the transfer lines was 280°C, the temperature of the ion source was 230°C, and the detector voltage was 1600V. The mass spectrometric detector (MSD) operated in full scan mode from m/z 35 to 350 with frequency 100 Hz.

Despite the fact that the nonpolar column can effectively separate a sample of organic nature into components to some degree, some of the samples with similar boiling points do not have corresponding peaks on the first chromatogram. Rocket kerosene represents a complex system with a wide boiling range. Previous investigations had shown that certain complex compounds present in its composition appear as one broad peak on the chromatogram obtained at the first stage of chromatography [11]. Only as a result of the presence of the focusing action of the modulator is it possible to separate the components of the kerosene further in the ^{2}D column according to differences in their polarities.

It is thought that a major factor affecting the retention time in gas chromatography is the column temperature. The temperature in the ^{1}D column is usually set somewhat higher than the temperature in the ^{2}D column so as to increase the volatility of the sample and the retention times of its components in the second column. However, according to the experimental results, when the temperature of the second column was 10-30°C higher than that of the first not only did the separation efficiency not decrease but information

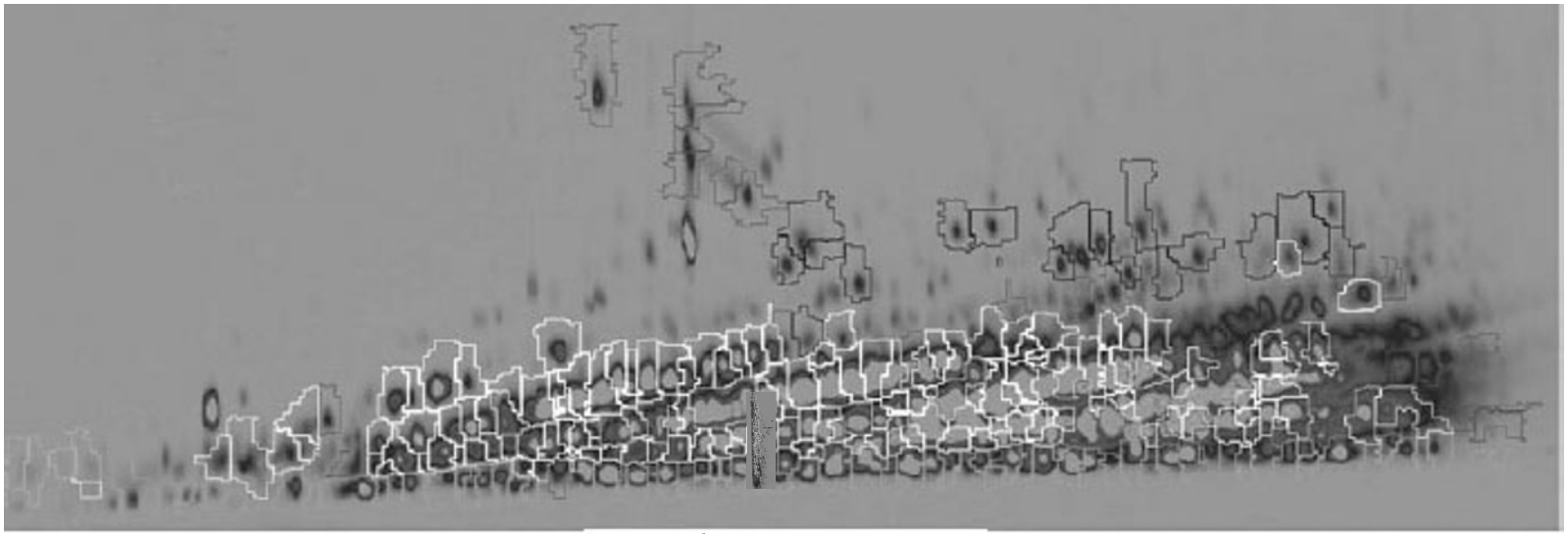

Fig. 1. Two-dimensional chromatogram of rocket kerosene obtained by the GC-GC/TOFMS method. (The homologs with various polarities are outlined in various colors.)

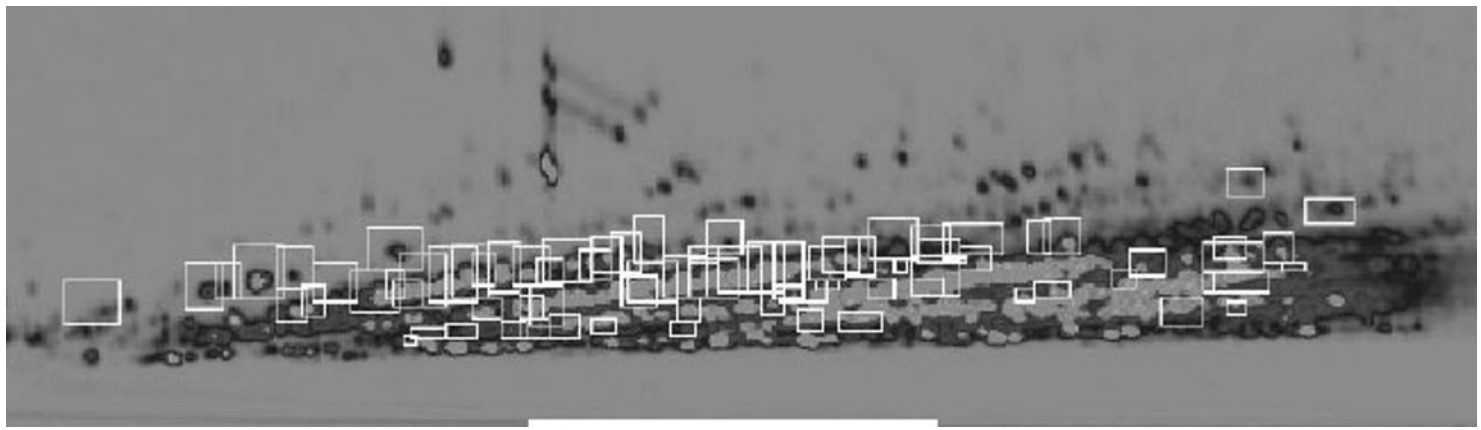

Fig. 2. Two-dimensional chromatogram of bicyclic alkanes present the sample of rocket kerosene. (The bicyclic alkanes are outlined in white.)

about the group and functional state of the sample could also be obtained from the chromatogram. Thus, the temperature program of the thermostat for the first column was 50°C (2 min) followed by heating to 180°C at a rate of 10°C/min, and in the second column it was 80°C followed by heating to 180°C at 2°C/min [12].

In general ionic chromatography homologs with identical functional groups are usually distributed along it in a specific order in the form of a belt whereas the regions corresponding to the isomers are in contact with each other in the form of "tiles." With temperature programming the retention times of the components were distributed on the chromatogram of the ^{1}D column according to their boiling points, and those of the ^{2}D column were distributed according to the polarity of the functional groups.

Since the retention time in the second column is short the GC-GC modulator is focused on the broad peak of the first chromatogram by programming the rate of increase of the temperature (2-5°C/min). In order to increase the degree of separation of the peaks in the present work a minimum heating rate of 2°C/min was used for the ^{2}D column. It was established that the longer the modulation time the smaller the number of fragments that can be identified, but at the same time the modulation time must not be very short. In the present work the selected time not affecting the efficiency of separation was 4 s, and the delivery time of the hot pulse was 0.25 s [13].

Table 1

Compound group		Number of individual substances	Content, vol. %	Total amount, vol. %
Paraffins	*n*-paraffins	17	4.95	17,1
	iso- paraffins	89	12.2	
Cycloalkanes	R-cyclohexane	76	1.6	23,8
	R-cyclopentane	13	1.88	
	others	18	3.32	
Bicyclic alkanes	R-decalin	78	17.5	45.6
	R-spiro[5,5]undecane	1	0.096	
	R-spiro[5,5]undecane	12	1.57	
	R-spiro[4,4]nonane	18	4.86	
	R-bicyclo[4,1]heptane	4	3.54	
	others	48	18.0	
Tricyclic alkanes		18	0.947	0.947
Alkenes		16	0.817	0.817
Aromatic compounds	benzene	50	0.62	3.01
	indene	20	2.39	
Oxygen-containing compounds	alcohols	29	1.71	4.5
	aldehydes	13	0.21	
	ketones	48	2.26	
	ethers	7	0.32	
Total		575	95,8	

Note. R – any alkyl radical.

Figure 1 shows the two-dimensional chromatogram of a sample of rocket kerosene analyzed by the GC-GC/TOFMS method. It can be seen that all the components were separated effectively according to their polarity and their molecular configuration. From the chromatogram it is possible to identify 575 peaks, whereas the normal GC-MS method (chromato mass spectrometry) only gives 141 peaks [10].

In the various regions of the chromatogram the peaks of the compounds of one homologous series are arranged in one line. Along the abscissa axis the compounds are arranged according to the boiling points, and along the ordinate axis they are arranged according to polarity. On the two-dimensional chromatogram the paraffins are located in the lower part in the form of a line. The following groups of compounds are located on the chromatogram from bottom to top: cycloalkanes, olefins, bicyclic alkanes, tricyclic alkanes, aromatic and oxygen-containing compounds. As well it can also be seen from Fig. 1 that the paraffins are arranged along the ^{1}D direction, i.e., according to polarity. In comparison, the cycloalkanes have longer retention times in the ^{2}D direction, and they increase with increase of the number of rings. The peaks of the aromatic compounds on the chromatogram are arranged strictly according to increase in the boiling point and the polarity of the aromatic ring.

The chromatogram for compounds of the bicyclic alkane group is presented in Fig. 2. It is seen that the isomers of one hydrocarbon are divided up according to the various values for the volatility and the polarity. Compounds with an identical number of carbon atoms are arranged in lines, while homologs are arranged as “tiles”. Each dot on the two-dimensional chromatogram corresponds to a compound that was detected automatically with a signal/noise ratio of 10:1. The mass spectrum and information about the structure of the sample can be obtained from the spectral data library.

In order to check the reliability of the data the peaks were identified several times, and it was established that the data from qualitative analysis of the sample are reliable. It was also confirmed by the results from construction of a three-dimensional chromatogram.

The content of each component was calculated by estimating the volumes of the peaks on the three-dimensional chromatogram. The 575 peaks identified during qualitative analysis were divided into seven groups: paraffins, cycloalkanes, bicyclic and tricyclic alkanes, alkenes, and aromatic and oxygen-containing compounds. The average number of carbon atoms in the compounds varied from 9 to 15. The results from quantitative analysis of the sample are presented in the table.

With appropriate choice of chromatographic column and optimum conditions the GC-GC/TOFMS method can thus be used for effective analysis of the components of a sample of rocket kerosene. Here qualitative analysis can be realized by identifying the structures of the various components, and quantitative analysis by estimating the areas of the characteristic peaks. As a result it was established that rocket kerosene contains the following components: paraffins, cycloalkanes, bicyclic and tricyclic alkanes, alkenes, and aromatic and oxygen-containing compounds. The components are present in the following proportions: paraffins 17.10%, cycloalkanes 70.3%, alkenes 0.82%, aromatics 3.01%, oxygen-containing compounds 4.5%.

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