Larisa Zakirjanova
Institute for Space Research of Natural Resources
larisa_53@mail.ru
Mirvari Jabrayilova
Institute for Space Research of Natural Resources
azerbaycan9195@mail.ru
Shahla Hajiyeva
Institute for Space Research of Natural Resources
elmitexnikisobe@mail.ru
Konul Yusupova
Institute for Space Research of Natural Resources
elxan207@gmail.com

Determination of the Chemical Composition of Oil and Gas

Abstract

Oil is a complex mixture of liquid organic substances in which various solid hydrocarbons, resinous substances and accompanying gases are dissolved. In the article various methods of separation of complex mixtures into simpler compositions were examined. The bulk of the oil components is also determined.

An important indicator in the identification of oil products is the amount of aromatic hydrocarbons in their content. In the methods used in the study of petroleum products in environmental objects, gas chromatographic analysis is preferred due to its highest selectivity, sensitivity and accessibility, using different types of detection. On the other hand, during the determination of PAHs in oils and middle distillates, in the chromatograms, the analyte appears against the background of the "naphthenic hump" and paraffins, which form fragments of molecules under electronic conditions, which overlap with each other. Fragments of molecules of substances analyzed in terms of ion mass are placed on them and their mass spectra are analyzed. When performing such analyses, it is practically impossible to identify, quantify, and accurately estimate the signal intensity of peaks associated with polycyclic condensed arenes.

Keywords: *distillation, phlegm, extraction, crystallization, molecular diffusion, adsorption, absorption, chromatography*

Introduction

Oil is a complex mixture of liquid organic substances in which various solid hydrocarbons, resinous substances and associated gases are dissolved. Separation of complex mixtures into simpler ones is called fractionation. Separation methods are based on differences in the physical, surface and chemical properties of the separated components (Syrkin, 2002, p. 92-96).

The following methods are used to separate oil into narrow homogeneous groups: distillation (atmospheric distillation and rectification, vacuum distillation and azeotropic distillation); adsorption (adsorption and chromatography); absorption (extraction) and crystallization. The most common fractionation methods are distillation. These include distillation and rectification. The essence of atmospheric distillation is that the mixture is continuously heated, with its components gradually distilled off from low-boiling to high-boiling (Ryabov, 2009, p. 17-47).

As the boiling point of the components increases, the heating temperature of the mixture being separated is also increased. By collecting fractions in predetermined temperature ranges and measuring their quantity, one can get an idea of the fractional composition of oil. The fractional composition of oil or oil products is understood to be the quantitative content of substances in oil that boil within certain temperature limits (Virzhichinskaya, 2009, p. 59-151).

Atmospheric distillation is used for rough separation into wide fractions. During factory refining of oil, the following fractions or distillates are collected:

1) gasoline (initial boiling point up to 170-200 ºC),
2) ligroin (170-200 ºC),
3) kerosene (200-270 ºC),
4) gas oil (270-350 ºC).

From these distillates, light oil products are further produced. The residue after collecting fractions up to 300-350 ºC is called fuel oil. Fuel oil is distilled into oil fractions under vacuum to prevent its thermal decomposition. Fractions are selected not by boiling point, but by viscosity. Oil distillates are divided into solar, transformer, spindle, machine, autol, and cylinder distillates as viscosity increases. The residue after distillation of fuel oil is called tar or semi-tar depending on viscosity (Ghosal, 2016, p. 13-69).

In accordance with the elemental composition, the bulk of oil components are hydrocarbons (RH). The gasoline fraction contains practically only three classes of hydrocarbons: alkanes, cycloalkanes, and benzene arenes. Bi- and tricyclic hydrocarbons make up a significant share in the kerosene and gas oil fractions. There are no unsaturated hydrocarbons with unsaturated bonds in crude oils. In addition to RH, heteroatomic organic compounds are present in the low-molecular part of the oil: oxygen (phenols), sulfur (sulfides, mercaptans), and sometimes nitrogen (amines) (Sorial, 2018, p. 1-17).

Their quantity is small in the low-boiling part of oil, they are mainly concentrated in fractions boiling above 350C (fuel oil). Azeotropic distillation also belongs to distillation methods. Mixtures of two mutually soluble liquids are called azeotropic, the boiling point of which is either lower than the boiling point of the low-boiling component, or higher than the boiling point of the high-boiling component (Gou, 2020, p. 1-13).

The essence of azeotropic distillation is as follows: a third, water-soluble, non-hydrocarbon component is added to the mixture being separated. In the presence of this substance, the initial components of the azeotrope change their vapor pressures differently when heated, i.e. have different boiling points. If the third component is close in volatility to the mixture being separated, then it forms an azeotrope with one of the components of the mixture (azeotropic distillation) (Guo, 2019, p. 297).

If the volatility of the third component is low, then it remains in the liquid phase and retains one of the substances being separated (extractive distillation). Molecular diffusion is used to separate the highest boiling substances. The method is based on the difference in molecular weights and depends on the relative evaporation rate of the molecules (Gupte, 2020, p. 127-149).

Adsorption methods. The essence of the method is that individual components of the mixture can be selectively and sequentially sorbed on one or another sorbent (absorber) and thus separated from the overall mixture. Then these components are desorbed unchanged in the form of individual fractions and can be studied separately. Desorption occurs in the reverse order of adsorption.

Chromatography. Adsorption chromatography is the process of separating substances on solid adsorbents by color. There are the following types of chromatographic analysis methods: gas-adsorption, liquid-adsorption, gas-liquid. Gas-adsorption chromatography is used to analyze gases and is based on the adsorption of gas components of a mixture on solid absorbers. Liquid adsorption chromatography is a method for separating liquid mixtures using solid adsorbents (silica gel).

Absorption. The essence of the method lies in the volumetric absorption of gases or vapors by a liquid (absorbent), leading to the formation of a solution. Absorption is used to separate gases. To isolate a component, a solution of the absorbent (absorbent) with the gas dissolved in it is sent for desorption.

Extraction is the process of extracting individual components from the feedstock by treating it with a selectively acting solvent (extractant). As a result of extraction, two immiscible phases are formed: an extract and a raffinate. The extract contains a solvent and highly soluble raw material components.

Crystallization. This method is used to separate substances with high melting points, i.e. solid hydrocarbons soluble in oil. Crystallization is carried out by freezing from solutions in a suitable solvent. The solvent must also be a precipitant for the substances separated by crystallization. It must dissolve high-melting components significantly worse than low-melting ones.

Determination and sampling of aromatic hydrocarbons in petroleum products by sulfation method

To separate aromatic hydrocarbons from oil products, let's consider the sulfation method. A rapid method for determining the amount of aromatic hydrocarbons in gasoline fractions is the sulfation method. When a hydrocarbon mixture is affected by sulfuric acid (concentration below 100 %) in the absence of alkenes, only arenes react with the formation of aromatic monosulfonic acids (Gupte, 2016, p. 363-378).

In this case, polysulfonic acids are not formed. In order to determine the content of arenes, the reaction of distillates with sulfuric acid is carried out at room temperature. Usually, the structure of the sulfuric acid formed corresponds to the structure of the arene. But in some cases, the reaction is complex and is accompanied by isomerization, disproportionation; this is mainly observed in polyalkylated arenes.

Arenes of petroleum distillates form water-soluble sulfuric acids. The solubility of sulfuric acids in petroleum distillates depends on the molecular weight and structure of the acids. Sulfuric acids formed from short side-chain arenes contained in the low-boiling fractions are insoluble in the distillate. They are all monobasic acids, and the difference between their properties is determined only by the structure of the side chain (Haleyur, 2019, p. 49-58).

Distillate-soluble sulfuric acids are derivatives of polycyclic arenes with fairly long side chains; dissolved in sulfuric acid, they completely pass into an acid layer where sulfuric acid is abundant. Sulfuric acids from long side-chain arenes are readily soluble in distillation. They can be isolated from treated distillates by adding ethyl alcohol.

The concentration of sulfuric acid is an important factor. A weak acid practically does not react with arenes. Fuming acid, on the other hand, can cause side reactions such as oxidation. In addition, fuming acid also affects other hydrocarbons – it causes dehydrogenation of six-membered naphthenes and reacts with isoparaffins.

Necessary equipment and materials: sulfator; sheath with drawn end; 98 % sulfuric acid; 10 % sodium hydroxide solution; calcium chloride; 1-2 l capacity separating funnel; apparatus for distillation with heated water vapor; concentrated sulfuric acid (monohydrate).

Work performance methodology. A well-washed and dried sulfator is fixed vertically on a tripod, the tap is closed, and using a funnel with an elongated end, 98 % sulfuric acid is carefully poured up to the "0" mark (so as not to spread along the walls of the sulfator). The acid is allowed to drain from the walls and its level is accurately recorded on the sulfator scale (Johnsen, 2007, p. 533-543).

After that, in the same way, 10 ml of the studied gasoline fraction is poured into the sulfator and its level is fixed. The sulfator is tightly closed with a plug, removed from the tripod, and the contents are carefully poured into the upper circular part, where it is shaken well for 1 minute, from time to time the tap should be opened a little to release the gases formed. After mixing, the sulfator is installed vertically on a tripod and the mixture should be kept for 1 hour. After this period, the volume of gasoline is recorded. The determination should be repeated twice, and the algebraic average of the results of both experiments is calculated. The volume share of aromatic hydrocarbons in the studied A0 fraction, in %, is found by a. the following formula:

$$A0= (V1-V2)/ 100V1 \quad (2.1)$$

where V1 – the volume of gasoline taken for sulfation; V2- is the volume of gasoline after sulfation. After measuring the volume of gasoline remaining after sulfation, the sulfuric acid gasoline layer is drained and the gasoline is washed in a sulfator with water, then with 10 % sodium hydroxide solution, then again with water until neutral, then dry. Transferred to a test tube and

dehydrated with calcium chloride. Dehydrated gasoline is taken to determine the second aniline point. In order to isolate aromatic hydrocarbons from the oil product, 200 ml of the studied fraction (heavy gasoline) boiling in the range of 150-200 ºC is introduced into the separatory funnel and 400 ml of sulfuric acid is carefully added. It is mixed and shaken in a separatory funnel for 0.5-1 hour. After precipitation, the lower (sulfuric acid) layer is carefully added to a 1.5 L round bottom flask and water (about 300 mL) is carefully added to prevent foaming during distillation. The flask is placed in the superheated steam distillation apparatus and the contents of the flask are exposed to the superheated steam. In this case, the mixture is decomposed by the formation of sulfuric acid and free hydrocarbon, steam distilled and collected in the receiver. The separated hydrocarbons are washed with water and soda solution, dehydrated over calcium chloride, and then collected in a column apparatus.

Determination of aromatic hydrocarbons in petroleum products by the method of aniline point determination

Equipment, reagents and materials: 15 ml test tube; a glass with a capacity of 750-1000 ml made of heat-resistant glass; long-handled thermometer, division degree 0.05; freshly distilled pure aniline (t.); 2 ml pipette; burettes with a graduation of 0.1 ml.

Work performance methodology. Method of equal volumes 2 ml of aniline and the gasoline fraction under study are placed in a clean and dry test bottle, tightly closed with a stopper with a thermometer and a stirrer inserted in it, and attached to a coupling immersed in a water bath. The product and aniline are obtained with 2 ml pipettes or burettes with a graduation of 0.1 ml.

The thermometer is placed so that the mercury ball is at the level of the dividing line between the layers of aniline and the product. The temperature of the water bath is slowly raised and the aniline product is continuously stirred with a stirrer. The temperature of complete mixing of liquids is noted (the solution becomes transparent). The heating is stopped and the water is expected to cool down slowly. When turbidity appears in the test tube, indicating the beginning of phase separation, the solution is stirred again with a stirrer.

At first the blur disappears with stirring, but then comes a moment of non-disappearing blur. The point of aniline is the highest temperature at which the turbidity does not disappear after mixing. The complete mixing and cloud point temperatures should not differ by more than 0.1 ℃. Determination of AN is repeated with a new sample of the investigated fraction. In parallel experiments, the discrepancy between AN should not exceed 0.2 ºC (12).

Conclusion

Maximum aniline points method. 2 ml of the studied fraction is placed in a 1.6 ml aniline test bottle and the temperature of complete dissolution is determined as described above. After that, another 0.2 ml of aniline is added to the mixture and the dissolution temperature is set again. It is usually higher than the first case. Aniline is added in increments of 0.2 ml until its decrease is noted after a certain maximum of the dissolution temperature. The maximum AN is recorded; it corresponds to the true value of the test product in aniline.

When there is a sufficient amount of material for each destination, new portions of the oil product and aniline should be taken.

References

1. Syrkin, A. M., Movsumzade, E. M. (2002). *Fundamentals of oil and gas chemistry*. USTU.
2. Ryabov, V. D. (2009). *Chemistry of oil and gas*. FORUM.
3. Virzhichinskaya, S. V., Digurov, N. G., Siyushin, S. A. (2009). *Chemistry and Technology of oil and gas.* FORUM.
4. Ghosal, D., Ghosh, S., Dutta, T. K. (2016). Current state of knowledge in microbial degradation of polycyclic aromatic hydrocarbons. *Microbiol*, 1369.
5. Sorial, G. A., Ghasemi, S., and Bazyari, M. (2018). Treatment technologies for PAH-contaminated sites: a critical review. *Environ. Monit. Assess*, 1-17.

6. Gou, Y., Zhao, Q., Yang, S., Qiao, P., Cheng, Y., Song, Y. (2020). Enhanced degradation of polycyclic aromatic hydrocarbons in aged subsurface soil using integrated persulfate oxidation and anoxic biodegradation. *Chem. Eng.*, 1-13.

7. Guo, Y., Rene, E. R., Wang, J., and Ma, W. (2019). Biodegradation of polyaromatic hydrocarbons and the influence of environmental factors during the cocomposting of sewage sludge and green forest waste. *Bioresour. Technol.*, 297.

8. Gupta, S., and Pathak, B. (2020). *Mycoremediation of polycyclic aromatic hydrocarbons. Abatement of Environmental Pollutants*. Elsevier.

9. Gupte, A., Tripathi, A., Patel, H., Rudakiya, D., and Gupte, S. (2016). Bioremediation of polycyclic aromatic hydrocarbon: a perspective. *Biotechnol,* 363-378.

10. Haleyur, N., Shahsavari, E., Jain, S. S., Koshlaf, E., Ravindran, V. B., Morrison, P. D. (2019). Influence of bioaugmentation and biostimulation on PAH degradation in aged contaminated soils: response and dynamics of the bacterial community. *Environ.*, 49-58.

11. Johnsen, A. R., and Karlson, U. (2007). Diffuse PAH contamination of surface soils: environmental occurrence, bioavailability, and microbial degradation. *Appl. Microbiol. Biotechnol.*, 533-543.

12. Analytical equipment for determining the composition of hydrocarbon raw materials and their processed products. www.nordwestlab.ru.