

**Y. Y. Bilynskiy, Dc. Sc. (Eng.), Prof.; O. S. Gorodetska, Cand. Sc. (Eng.), Assist. Prof.;
V. V. Krotevich**

REVIEW OF THE METHODS FOR DETERMINING SULFUR CONTENT IN PETROLIUM PRODUCTS

The paper reviews main methods for determining sulfur content in petroleum products and develops their classification.

Keywords: *methods for determining sulfur content, petroleum products, X-ray fluorescence, spectroscopy.*

Introduction

Strategy of the development of oil refining and petrochemical industries involves improving the quality of petroleum products and bringing it to the world standards. Sulfur is one of the elements that is a natural component of crude oil and has negative influence on the quality of petroleum products. Sulfur compounds give unpleasant smell to petroleum products, lead to corrosion of the equipment and poison expensive oil refining catalysts [1]. During combustion of petroleum products sulfur oxides are emitted, which pollute the atmosphere.

At present, the requirements to the sulfur content in automobile gasoline and diesel fuels are constantly growing throughout the world. According to the “old” state standard of Ukraine ДСТУ 4063-2001 for gasoline of brand A - 95 of Ukrainian production, sulfur content should not exceed 0.015 % or 150 mg / kg. According to ДСТУ (State Standard of Ukrain) 4839-2007, sulfur content for gasoline of brand A-95-EURO with improved quality, that has European tolerances, should not exceed 0.005 % or 50 mg / kg, which satisfies standard norms of EURO 4. According to the current standard norms EURO 5 sulfur content in the “ninety fifth” gasoline should not exceed 0.001 % or 10 mg / kg [2].

The aim of this paper is to describe main methods for detecting sulfur and to elaborate classification of the methods on the basis of determining physical, chemical and optical parameters of the object under study.

Main part

On the basis of the conducted review of the methods for determining sulfur content in petroleum products [3 – 6] we propose a classification based on five classification criteria: according to the type of sample preparation, according to the informative parameter, according to the type of radiation source, wavelength range and the type of detection (Fig. 1).

Parameters used for obtaining information about the object under study include optical, electrical parameters, parameters of ionizing radiation, the amount of substances formed as a result of chemical reactions, color change of the indicator. As a result of light absorption by the object under study, in visible, ultraviolet and infrared regions of the spectrum the following optical parameters are measured: light emission intensity, refractive index, indices of absorption and dissipation. Sulfur, the content of which is determined, is converted to a compound by means of a chemical reaction in a solution. The amount of this compound is measured easily and is an informative parameter. Other informative indices include electrical parameters, ionizing radiation parameters and color change of the indicators.

According to the type of sample preparation the following methods are distinguished: methods based on sulfur oxidation followed by detection of oxides, methods based on sulfur reduction to H_2S and methods without preparation. Methods based on sulfur oxidation include bomb method, lamp method, methods of combustion in oxygen-hydrogen burner, of combustion in oxygen, in quartz tube, oxidative combustion and electrochemical detection, oxidative microcoulometry and UV

fluorescence.

In the bomb method a sample weight of the test product is burned in a calorimetric bomb filled with compressed oxygen. Sulfur dioxide, created as a result of combustion, is absorbed by an alkali, the formed sulfites are oxidized to sulfates and then sulfur is detected gravimetrically by precipitation with barium chloride in the form of BaSO_4 . The method is intended for analyzing products that are not burned completely in the lamp: lubricating oils with additives, additives, grease lubricants. The method is used for products with low volatility that could be weighed accurately in the open crucible but cannot be used for light petroleum products and used oils. The lower limit of sulfur content to be determined is 0.1 % [7].

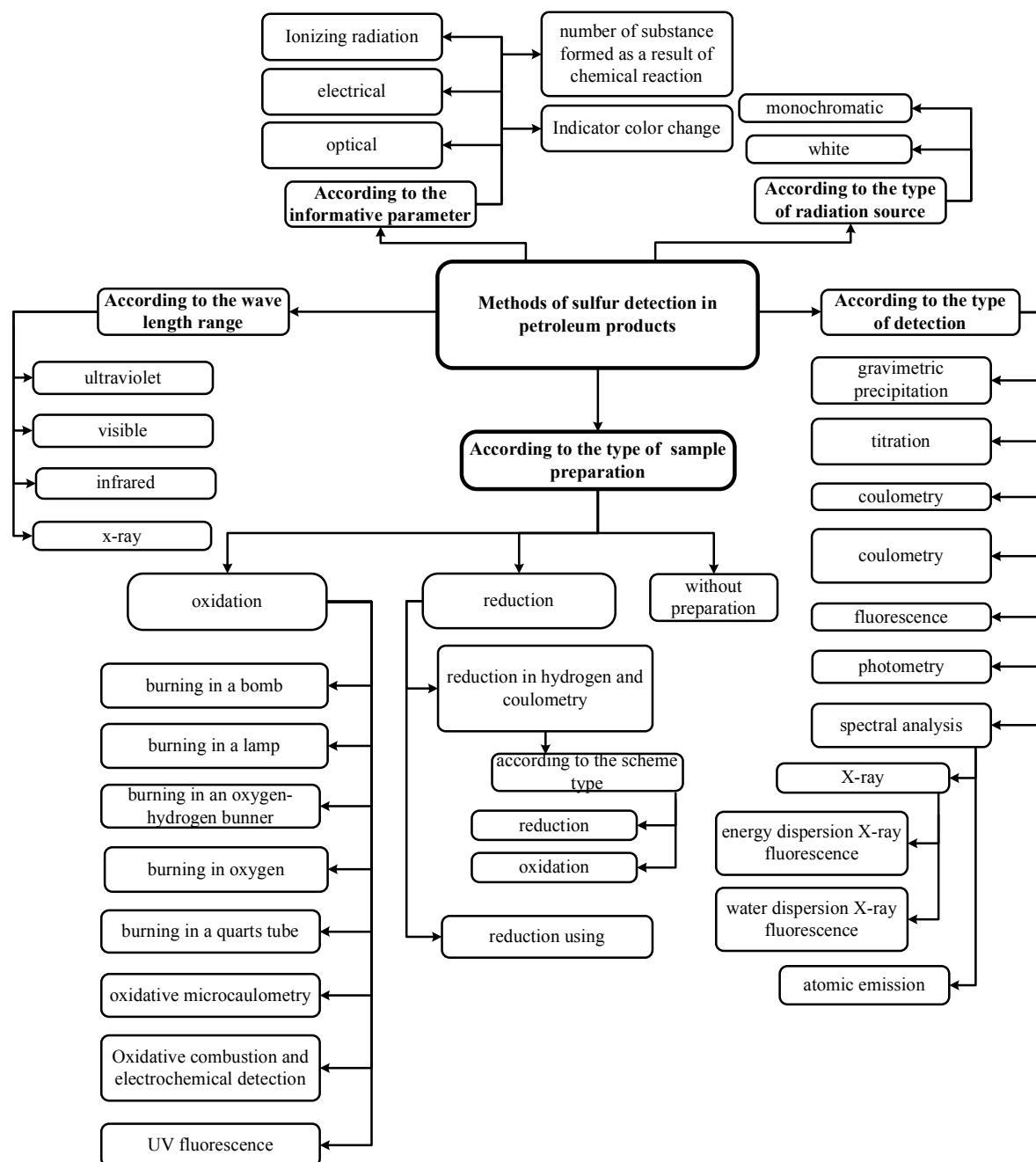


Fig. 1. Classification of the methods for sulfur detection in petroleum products

In the lamp method the sample is burned in a closed system using a lamp with cotton wick. The created sulfur dioxide is absorbed and oxidized to a sulfuric acid by treatment with hydrogen peroxide. The solution is blown with air to remove the dissolved carbon dioxide. Sulfur is detected by the amount of sulfate, obtained by titration with sodium hydroxide or gravimetrically by

precipitation in the form of BaSO_4 . Petroleum products, that are not burned in a pure form, burn poorly or form strong soot are burned with dilution. By means of the lamp method sulfur is detected in light petroleum products (gasoline, kerosene) as well as in other liquid petroleum products that are burned completely in the lamp of the apparatus. The lamp method is not used for petroleum and oils with additives. The lower limit of sulfur detection in petroleum products for its mass fraction should be no less than 0.01% [8].

The method of burning in a oxygen-hydrogen burner is intended only for analyzing liquefied gases and is based on a complete combustion of the sample. Instead of the lamp, an oxygen-hydrogen burner is used, which enables quantitatively burning of not only liquid hydrocarbons but also gases including liquefied gases. The method is extremely labor-consuming, requires the use of compressed gases (oxygen and hydrogen), mercury and bulky glass equipment. Its quality is rather low [9].

The method of burning in oxygen is intended for dark petroleum products boiling at the temperature above 177°C and containing not less than 0.06 % of sulfur. It is also used for oils with additives. It is possible to analyze coke with sulfur content up to 8 %. Alkaline and alkaline earth metals, zinc, phosphorus, lead do not prevent from detection. In a variant of the method with subsequent titration by an iodide, repeatability depends on the range: in the range of 0 – 0.5 % it is 0.05 %; reproducibility in the same range is 0.08 %. Chlorine has an interfering effect in concentration above 1 % and nitrogen in concentration above 0.1 %. In a variant of the method with subsequent infrared detection in the range of 0 – 0.5 % repeatability is 0.04%. Reproducibility in this range is 0.13 % [3]. Nitrogen does not interfere with detection. Chlorine does not affect detection in the concentration up to 1 %.

In the method of burning in a quartz tube test sample of the product is burned in a quartz tube at the temperature of $900 - 1200^\circ\text{C}$ with subsequent absorption of the combustion products and titrimetric finish. For combustion air is used. Combustion products are absorbed by the solution of hydrogen peroxide that oxidizes sulfur combustion products to sulfates. The range of determining sulfur content is 0.1 – 5.0% [3]. This method is used for the analysis of dark petroleum products including oils and residual petroleum products as well as coke and sulfur-containing additives.

The method of oxidative microcoulometry is intended for the analysis of light hydrocarbons with boiling temperature range of $26 - 274^\circ\text{C}$ in sulfur concentration range from 3.0 to 100 ppm. This method is not used for samples containing heavy metals. In this method liquid test sample is injected into gas flow. During combustion sulfur is oxidized to dioxide that is supplied to titration cell filled with an electrolyte. Sulfur dioxide is titrated by triiodite ions generated in the cell under the action of current. The amount of electricity consumed for triiodite generation is directly proportional to the amount of sulfur dioxide that enters the titration cell. The lower limit of quantitative determination of sulfur by this method is 3 mg / kg in gasoline and 5 mg / kg in diesel fuels [3]. In this case sulfur detection requires special attention to the cleanliness of the equipment and reagents.

In the method of oxidative combustion and electrochemical detection the test sample is burned in oxygen with formation of oxides but instead of coulometric titration cell electrochemical detector is used that is an amperometric device. However, this method is not recommended by international committees for sulfur detection in low-sulfur fuels as in interlaboratory tests the method showed the worst accuracy characteristics [3].

The principle of UV fluorescence method is as follows. The test sample is completely burned in oxygen with formation of oxides. Simultaneously, during combustion of hydrocarbons carbon dioxide and water are formed. Water is removed by passing the gas flow through a membrane dryer, the action of which is based on diffusion of water molecules through a tubular polymeric material permeable for water but not permeable for gas. The diffused water is removed by a counterflow of dry gas. The dried gas, formed after test sample combustion, enters an ultraviolet detector where it is radiated by ultraviolet light. Molecules of SO_2 absorb the energy of ultraviolet radiation and pass into excited condition. When returning to stable condition, they emit quanta of light with wavelength that is different from that of exciting light. The emitted energy is registered by a photomultiplier and is

converted into electric signal. The method of UV fluorescence is “dry”, i. e. it does not require water solutions which are capable of active absorption of sulfur oxides [10].

The methods, based on sulfur reduction to H_2S , include the method of reduction in hydrogen, ratiometric coulometry and reduction with Raney nickel.

The method of reduction in hydrogen and ratiometric coulometry are used for sulfur detection in petroleum products in concentration range from 0.02 to 10.00 mg / kg. The method is based on reduction of sulfur-containing compounds to hydrogen sulphide in hydrogen flow with subsequent quantitative detection of the formed hydrogen sulphite by reaction of the coloured lead sulphide. The amount of the formed brown-coloured lead sulphide, proportional to the initial sulfur content, is determined by means of measuring it photometrically in the reflected light. Schemes of two types are used: reduction scheme and oxidation scheme. A drawback of the method is as follows: the created carbon is deposited at the output of the pyrolysis tube and absorbs the created hydrogen sulphide, which invalidates detection results. Materials that can be analyzed using this method, include solvent petroleum spirit, kerosene, spirit, steam condensate, various distillates, fuel for jet engines, benzol and toluol [3].

Method of recovery with Raney nickel is based on binding sulfur compounds by a highly reactive pyrophoric nickel formed by etching the alloy of nickel and aluminum with hydrochloric acid (Raney nickel) with nickel sulfide formation. As a result of nickel sulfide decomposition by the acid, hydrogen sulfide is formed. It is absorbed by sodium hydroxide and then detected by mercuric acetate titration with dithizone as an indicator. The range of sulfur detection by this method is from 0.2 to 250 mg / kg [11]. Disadvantages of this method are inability to determine quantitatively nickel sulphide and the presence of significant amounts of olefins in the test sample, which can form a polymer film on the surface of pyrophoric nickel blocking the active surface.

According to the type of radiation source, sulfur detection methods are divided into those using monochromatic or white radiation. Respectively, different types of emitters are used such as semiconductor lasers, light bulbs, LEDs.

Depending on the wavelength, the electromagnetic radiation spectrum, which acts on the test sample, is divided into several regions: an X-ray region – 0.01 – 10 nm, ultraviolet region – 10 – 400 nm, visible region – 400 – 700 nm and infrared region – 700 – 1100 nm.

According to sulfur detection in the test sample, a gravimetrical precipitation method is distinguished, in which sulfur amount is determined according to the mass of substance obtained as a result of precipitation under the action of precipitating agent. Detection can also be performed by titration based on measuring the volume of agent solution of the exactly known concentration spent for reaction with sulfur. Sodium hydroxide, potassium iodate, silver nitrate, solution of potassium iodide and sodium azide are used as reactive agents. Sulfur oxides are detected by their absorption of a definite radiation from the above-mentioned types. The method of oxidative coulometry is intended for the analysis of petroleum gases and is based on determining the quantity of electricity spent during the electrochemical reaction. Detection can also be performed by the method of ratiometric colorimetry that measures not the absolute value of optical density but its first derivative – color intensity growth rate, which is the reason for the method being named ratiometric. One of the most prospective detection methods is fluorescence – light emission by a substance after absorption of radiation. It is caused by transition of molecules from the excited singlet state into the basic state. The emitted energy is registered by a photomultiplier and converted into electric signal.

Photometrical method is based on measuring the absorption of radiant energy of the test substance. Absorption of radiant energy is proportional to sulfur concentration and, therefore, the character of absorption spectrum serves as qualitative sign of the presence of sulfur and the absorption value is used as a quantitative characteristic making it possible to determine sulfur content.

Spectral methods use X-ray radiation based on photoelectric effect. Photons of the exciting radiation liberate electrons from internal K- and L-shells of atom with formation of vacancies. When

a vacancy is filled with electrons, passing from external shells, atom emits radiation with energy corresponding to these electron transitions. This process is called X-ray fluorescence and the method of analysis based on measuring the intensity of characteristic fluorescence radiation for given wavelengths or energies – X-ray fluorescence spectrometry.

For sulfur detection by this method a liquid sample of the petroleum product is placed into a cylindrical container with bottom made from a thin film permeable for X-ray radiation. Then the sample is radiated with X-ray tube [2].

Methods of X-ray fluorescence spectrometry are divided into two groups:

- methods, based on spectral decomposition of characteristic radiation according to energies and measuring the intensity of signals for given values of energy of this radiation, are called energy dispersive X-ray fluorescence (EDXRF) methods;

- methods, based on measuring the intensity of characteristic radiation for given wavelengths of this radiation, are called wave dispersive X-ray fluorescence (WDXRF) methods [12].

Operation principle of the devices based on EDXRF method is as follows. X-ray tube radiation is directed to the test sample from below at a certain angle. As a result, there is a fluorescence radiation of sulfur and dispersive radiation that are later registered by a detector. Directly near the detector port a filter is installed passing $K\alpha$ line of sulfur and cutting off low-energy component of the tube radiation spectrum.

The detector registers X-ray quanta. When X-ray photons are absorbed, in the detector electric pulses are generated, their amplitude being proportional to the energy of the registered photons.

The pulses are amplified by a linear amplifier and enter amplitude analyzer where the number of pulses with a definite amplitude, proportional to the radiation energy, is calculated.

As a result, a characteristic spectrum of the sample is obtained. Peak of such spectrum corresponds to $K\alpha$ line of sulphur and is maximal at 2.3 keV. For signal registration a detector with sensitivity in the region of $K\alpha$ line of sulfur is used.

In Ukraine, Analyzer Lab-X 3500 of Oxford Instruments company (UK) was introduced into the State Register of Measuring Means. This device provides sulfur detection from 5 – 10 ppm to 5.5%. But even recent models do not provide the desired accuracy at low concentrations of sulfur and cannot be used for control of environmentally harmful gasoline and diesel fuels [12].

The operating principle of devices, based on WDXRF method, is as follows. The sample is also subjected to X-ray radiation, whereby secondary radiation of the sample is directed through a collimator, by a parallel beam, to the diffraction crystal positioned at an angle to the detector.

From the flow of secondary radiation, radiation with a wavelength corresponding to the element to be detected is separated (for sulfur - $K\alpha$ line with a wavelength of 0.5373 nm). To separate emission with the required wavelength, angle θ , at which the crystal is positioned, is determined.

There are WDXR analyzers that can measure full spectrum of the sample and analyzers with rigidly mounted crystals. The first make it possible to detect many element, the others – a limited range depending on the crystals used.

All the X-ray fluorescence methods have a number of advantages: high rapidity (from 2 to 5 minutes for one detection), absence of the necessity of sample preparation, wide range of sulfur content to be determined, good reproducibility. The disadvantages include high probability to obtain unreliable results, especially in low sulfur concentration range, unless you strictly follow all the recommendations of the method and all the instructions of the device manufacturers.

Atomic emission spectrometry with inductively coupled plasma (ICP-AES) is a method that has unique capabilities for detecting a large number of elements in a single sample. The sensitivity of sulfur detection by this method is low. The main purpose of ICP-AES is simultaneous detection of a large number of elements (up to 80 elements), including sulfur. The advantages of atomic-emission method include high measurement speed (less than 1 min) and measurement of low concentrations of the elements.

Conclusions

Analysis of the materials of scientific-technical literature shows that at present there is a wide range of sulfur detection methods. International community carries out regular interlaboratory research on the results of detecting elements in various objects by various methods in order to study their applicability and accuracy characteristics. On the basis of the obtained data, conclusions have been made that the oxidative methods and sulfur reduction methods require preparation of additional solutions, they are time-consuming and not sufficiently accurate.

The majority of modern instruments use spectral methods and UV fluorescence that are capable to detect lower concentrations of sulfur. At the same time, disadvantages of the methods include the fact that when working with X-ray analyzers, the intensity of secondary radiation measurements is influenced by permeability of the environment it passes through, which depends on its composition, temperature and pressure. Another source of errors could be water dispersed in the sample. Suspended water droplets are attracted to the bottom of the cell electrified under the influence of high-energy radiation and absorb both exciting and secondary radiation. This should be paid special attention to in the analysis of oils with low sulfur content.

A prospective sulfur detection method is the photometrical method distinguished by high accuracy, sensitivity to extremely low concentrations of sulfur content, reproducibility of the results, the possibility of simultaneous detection of a large number of elements in a single sample.

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Bilynskiy Yosyp – Dc. Sc. (Eng.), Prof., Head of the Department of Electronics.

Gorodetska Oksana – Cand. Sc. (Eng.), Ass. Prof. of the Department of Telecommunication Systems and Television.

Vinnitsia National Technical University.

Krotevich Vitaliy – Engineer.

LLC “Ukrghostech,” State Enterprise.