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New Coulometeric Method for Determination of the Chemical Compositions of Refinery Waste

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ORGANIC sulfur compounds are natural components of crude oil. The presence of these compounds is undesirable, as they cause corrosion of equipment and contaminate the atmosphere during combustion. Sulfur compounds ruin expensive catalysts and release sulfur oxides into the atmosphere when burned, thereby creating environmental problems. There fore, modern methods are needed to detect, identify and measure the concentrations of sulfur contents, water, and other elements in petroleum products. This work proposed a method for the quantitative analysis of petroleum and petroleum waste, including refinery sludges, based on the coulometry method. The present article describes the methods to determine the total amount of sulfur in the waste oil and the number of hydrocarbons in the viscous oil wastes. Additionally, Karl- Fischer method was adapted to measure the content of water in crude oil. In our work reported here, a titration coulometric reagent administration and potentiometric detection using ion-selective electrodes has been worked out and applied for the determination of sulfur and water concentration in crude oil samples.

Keywords: Coulometry, Crude oil, Analyses, Karl-Fischer method.

Introduction

The petroleum products are essential in the modern world and include high-quality gasoline, diesel fuels, various lubricating oils, and synthetic additives, rubber products, and synthetic rubber. It is difficult to find a branch of the national economy in which products from the petrochemical industry are not be used. One of the most important indicators of oil quality, along with fractional composition, viscosity, and density, is the total content of sulfur, which is variable. For example, the sulfur content in petroleum from the Bashkir region reaches 3%, and in Uzbekistan, it reaches 6%. It is present not only in the free state but also in the composition of sulfur compounds, resinous substances (hydrogen sulfide, mercaptans, aliphatic sulfides, disulfides, thiophenes), and both volatile and highly volatile compounds are organic sulfur compounds are natural components of crude oil. During the processing of oil, the thermal effect causes sulfur and its compounds to exists petroleum products in various concentrations. The presence of sulfur compounds makes it difficult to use petroleum fractions as fuels and lubricating oils and for processing into petrochemical products. The presence of these compounds, especially H_2S, is undesirable because they corrode equipment, ruin expensive catalysts used for refining oil, confer an unpleasant smell to oil products, and pollute the atmosphere during combustion, thereby creating environmental problems [1]. Increasing environmental protection requirements impose stringent restrictions on emissions of harmful substances into the atmosphere, including sulfur compounds. A variety of methods for detecting sulfur have been developed and range from classical chemical ones (e.g., burning in a bomb or lamp followed by a titrimetric or gravimetric measurement) to modern instrumental ones

(e.g., ultraviolet and x-ray fluorescence techniques) [2,3]. However, development of modern methods is needed for detection and measurement of sulfur compounds along with other elements (e.g., V, Fe, Ni, Ti, Cr, Co, Ca, Na, K, Si, P, Ge) in petroleum products [4]. The goal of this study is to develop methods for the quantitative analysis of petroleum products and oil wastes, including refinery sludge. To achieve this goal, i) a method was developed to measure the total amount of sulfur in oil waste; ii) a method was developed to measure the number of hydrocarbons in viscous oil waste, and iii) KarlFischer's method was adopted to measure the water content in crude oil.

The UV fluorescence technique is the second most widely used and accepted after infrared. It is very sensitive and requires no use of solvents, but it is important to remember that should the ratio of aromatic to aliphatic (or aromatic to total hydrocarbons) change due to, for example, the inclusion of new oil streams from different fields, because the oil is not distributed perfectly in the sample. It is no stable emulsion. So that not able to catch a representative amount of oil in a 1ml cuvette [5].

However, most of these methods do not have the expresses necessary for industrial use. In addition, it is not always clear that the determination of sulfur is correct.

As compared to conventional techniques for conducting chemical analysis, coulometry offers several advantages. First, there is no need to prepare standard solutions with known concentrations, as they are not used in this method. All that is required is the preparation of the background electrolyte and weighing of the sample. The titrant that is used in the reaction is prepared by the electrochemical method by passing the current through the coulometric cell. Calibrating the device is not necessary, because the data are absolutely and directly proportional to the amount of electricity that has been done (according to Faraday's law). This number must be calculated exactly. The end of titration can be determined when a certain potential difference, current strength, or spectrophotometric is reached [6]. Determination of the equivalence point can be carried out by potentiometric, amperometric, spectrophotometric, and other methods with high accuracy.

Experimental

Reagents and materials

The reagents and materials used in this study were as follows:

Potassium iodide; glacial acetic acid; sodium acetate; distilled water; laboratory filter paper; tetrachloromethane (ppm); oil sludge; diethyl ether (ppm); and titer of Fischer's Reagent were purchased from (SIGMA-ALDRICH) in Germany.

Instruments

An automatic coulometric Karl Fischer titrator supplied by Mettler Toledo (Greifensee, Switzerland) Model DL37 was used in the study of the reagent performance and water measurements.

Coulometric combustion analyzer ECS-1000 (German), PH meter model metrohm 713, water bath with magnetic stirrer model TKF (India), Furnace Oven model 1050 (Italy).

Preparation of solutions

To make the buffer (absorbent) solution, 57 mL of glacial acetic acid was dissolved in 500 cm^3 of water. Next, 7.7 g of ammonium acetate (or sodium acetate) and 16.6 g of potassium iodide were added. The volume of the solution was adjusted to 1000 cm^3 with water, and the solution was stirred. The error in the preparation of the solution was not more than 2.0%. pH of the solution was 3.7, and its half-life was 1 month [7].

Preparation of coulometer

When using the coulometer, the following steps were followed: 1) Turned on the oven in accordance with the instruction manual to warm it to a temperature of 1100 °C; 2) Filled the coulometric cell with a buffer solution of the electrolyte; 3) Placed the electrodes in the appropriate sockets of the coulometric cell; 4) Placed the rod of the magnetic stirrer in the measuring cell; 5) Turned on the magnetic stirrer; 6) Turned on the pump for forced air supply; and 7) Connected the Colorimeter EXPERT-006 according to instructions in the operation manual.

Measurement conditions

The measurements were taken under the following conditions: air temperature 15–25°C; relative air humidity not > 90% at 25 °C; atmospheric pressure 84.0–106.7 kPa; voltage in the network 220–110 V; and frequency of alternating current 50–10 Hz.

Measurement of the mass concentration of sulfur in petroleum products

Structurally, coulometric analyzer consists of an oven that provides heating up to 1200°C. A quartz tube placed inside the furnace is connected to the coulometric cell of the measuring transducer, which includes a galvanostat and a coulometer. The device also includes an electrochemical cell consisting of anode and cathode chambers separated by a porous glass filter and a magnetic stirrer [8]. Titration of the analyte is carried out in an electrochemical cell that contains a pair of generator electrodes and an indicator electrode used for potentiometric determination of the endpoint of the titration. The system also requires an electrolyte for generating the titrating reagent and a sample of the analyte [9].

Results and Discussion

A Measure of the mass content of sulfur in petroleum products

A fundamentally different approach is the use of oxidation-reduction titration. When sulfur and its compounds are burned at a temperature on the order of 1000 °C, the main product is not sulfuric anhydride but sulfur dioxide (SO_2), which, when dissolved in water, can be measured coulometrically. Oxygen combustion with coulometric detection (i.e., oxidative microcoulometry) is regulated in ASTM International - ASTM D3120-03a Standard test method for trace quantities of sulfur in light liquid petroleum hydrocarbons by oxidative microcoulometry [10].

With this method, sulfur can be measured in the concentration range of 3.0 to 100 ppm in liquid hydrocarbons boiled from 26 to 274 °C. Halogens (chlorine, bromine, iodine) do not interfere when present in concentrations 10 times higher than the concentration of sulfur. Nitrogen does not interfere when present in 1000-fold excess. However, the method is not applicable to samples containing heavy metals (nickel, vanadium, lead, etc.) at concentrations above 500 ppm [11]. The liquid sample is injected into a gas stream consisting of 80% oxygen and 20% inert gas (argon or helium). During combustion, sulfur is oxidized to the dioxide that enters the titration cell filled with electrolyte (an aqueous solution of acetic acid with the addition of potassium iodide and sodium

azide). Sulfur dioxide is titrated by the triiodide ions generated in the cell under the action of current [12]. These processes can be described by the following equations:
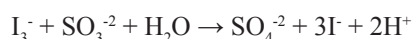
Pyrolysis of sulfur compounds:

$$R\text{-}S + O2 \rightarrow SO_2 + \text{combustion products}$$
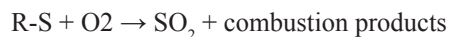
Generation of iodide at the anode:

$$3I^- \rightarrow I_3^- + 2e^-$$
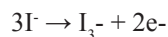
Reaction to free iodine with sulfite ion in the cell volume:

$$I_3^- + SO_3^{-2} + H_2O \rightarrow SO_4^{-2} + 3I^- + 2H^+$$

Because one triiodide ion reacts with one SO_2 molecule, the amount of electricity spent to generate the triiodide is directly proportional to the amount of SO_2 entering the titration cell. Thus, under the condition of 100% conversion of all sulfur contained in the sample into dioxide, the method is absolute and does not require calibration, and only the amount of electricity is measured. However, under conditions of a highly oxidative environment at high temperature, some of the sulfur is oxidized to trioxide SO_3, which does not react with the titrant. The amount of SO_3 formed depends on the nature of the sample, in particular, on the fractional composition and nature of the sulfur-containing compounds. Therefore, in order to obtain an adequate calibration, it is recommended to use calibration samples that are close in matrix composition to the analyzed sample [13]. Measurement of sulfur by this method requires special attention to the purity of the equipment and reagents used. The purity of the gases used must be at least 99.995%.

Based on these principals, the system of practical determination of sulfur in hydrocarbons based on the coulometric determination of SO_2 gas released during the combustion of a hydrocarbon was created. At the moment, the coulometer is capable of detecting 1 μg of sulfur. As can be seen in Fig. 1 and 2, respectively. The study of the influence of the weight of the sample on the readings of the devices "Sulfur Analyzer". Measured sample a standard sample for determining the mass fraction of sulfur. Mass fraction of sulfur is 2.5%. The furnace temperature is 1100 C°. The results of the measurements are shown in Table 1.

TABLE 1. Study of the influence of the weight of the sample on the readings of the instruments "Sulfur Analyzer".

№	V mL	Result Experiment %	Result Theory %	Average %
1	5	1,5576	2,2	70,80
2	5	1,5652	2,2	71,15
3	5	1,4461	2,2	65,73
4	10	1,5810	2,2	71,86
5	10	1,5708	2,2	71,40
6	10	1,5632	2,2	71,05
7	15	1,5960	2,2	72,55
8	15	1,5848	2,2	72,04
9	15	1,6184	2,2	73,56
10	20	1,6526	2,2	75,12
11	20	1,6046	2,2	72,94
12	20	1,6336	2,2	74,25
13	30	1,6391	2,2	74,50
14	30	1,6114	2,2	73,25
15	30	1,6269	2,2	73,95
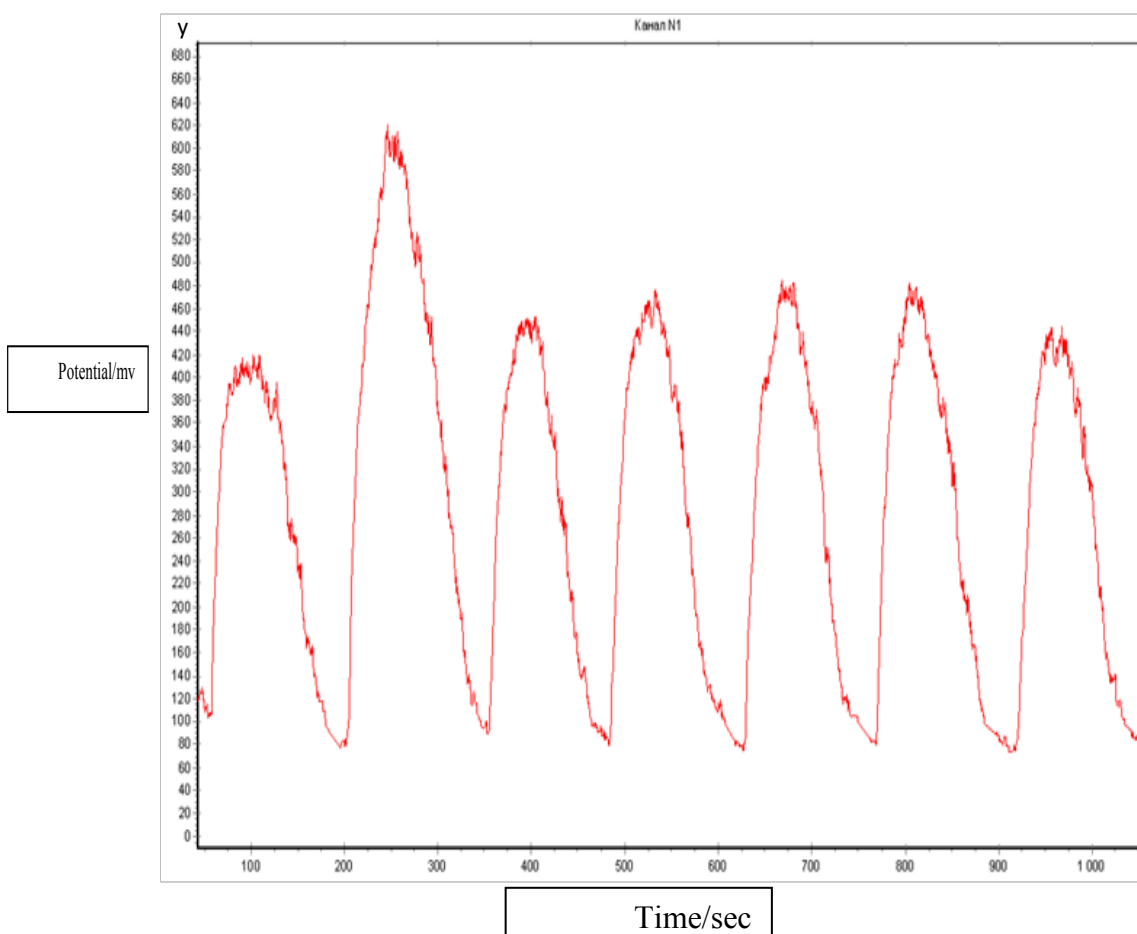
Fig. 1. Coulometric titration curves for the determination of SO2 in standard samples. Sample weight 10 mg.

Results of our experiments showed that furnace temperature of 1100 °C and sample weight of 10–30 mg were the optimal conditions for analysis. With a sample weight > 40 mg, oxidation of the sample is incomplete, resulting in a significant amount of soot contaminating the quartz tube and solution. Currently, the sensitivity of the instrument is 50 ppm, which corresponds to 1 mg of sulfur at a sample weight of 20 mg. To improve the sensitivity of the device, it is necessary to increase the weight of the sample, which requires solving a number of problems. When burning in a current of oxygen, the weight of the sample is 100–200 mg, and at low sulfur contents, it reaches 500 mg. An increase in the weight of the sample to 200 mg will reduce the boundary of the sulfur content to 5 ppm [14,15].
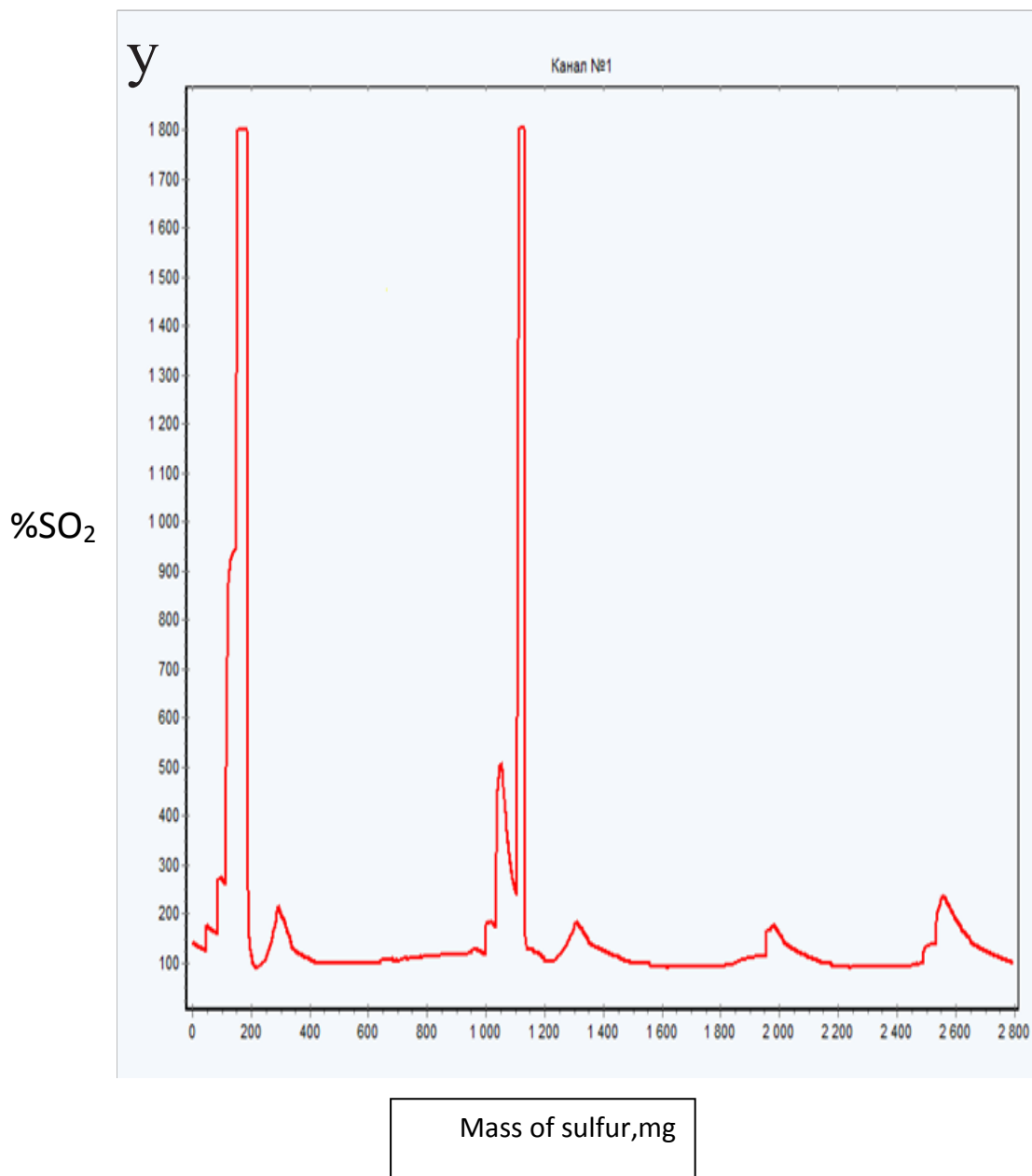

Fig. 2. Coulometric titration curves for the determination of SO2 in standard samples. Sample weight 5 mg.
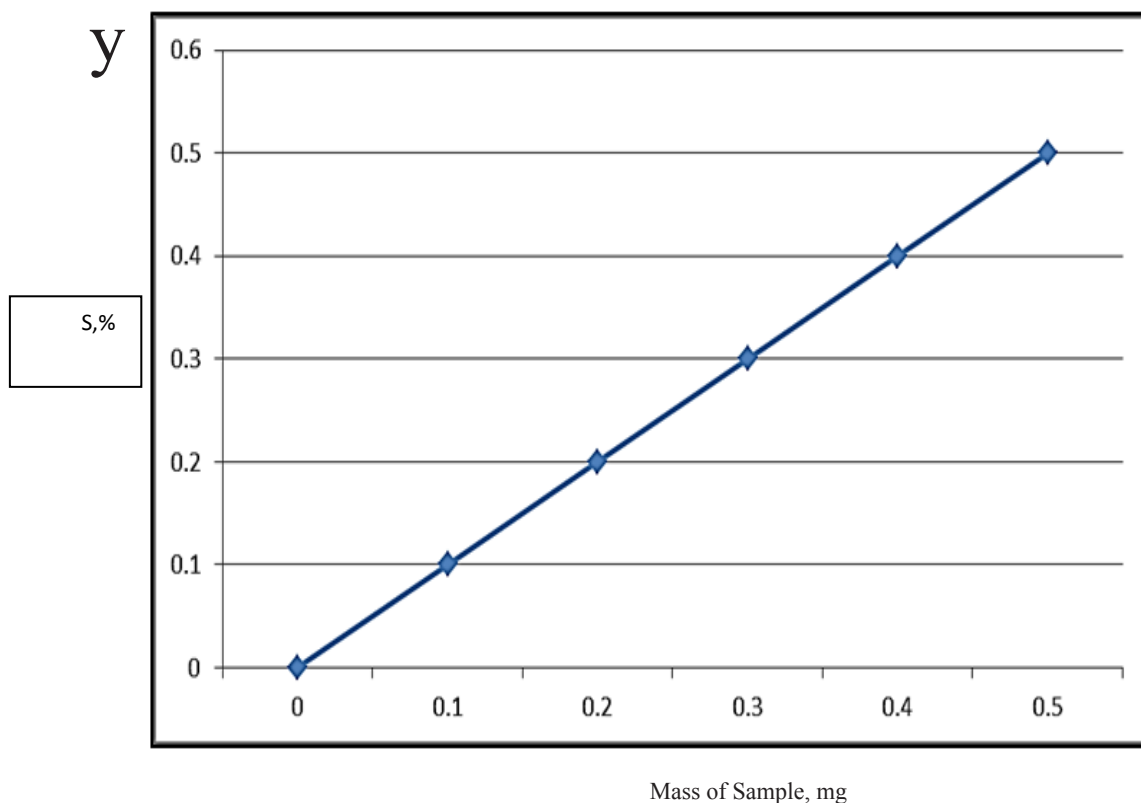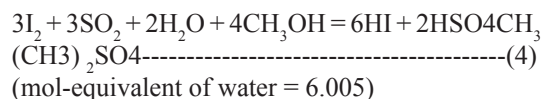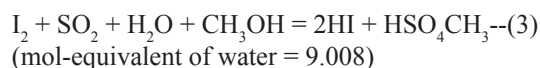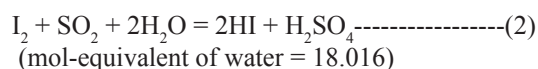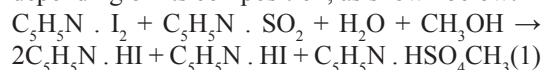
y

Mass of Sample, mg

Fig. 3. Dependence of the sulfur content in the sample on the sample weight (in mg). The sample weight is 20 mg.

Measurement of water content in oil and petroleum products using the method of Karl Fischer

In this study, we adapted Karl Fisher's method to measure the water content in crude oil. During the first stage of development of the technique, the stoichiometry of the interaction and the reason for the instability of the reagent were studied. Various analytic reactions can occur in the Fischer reagent depending on its composition, as shown below:

$C_5H_5N \cdot I_2 + C_5H_5N \cdot SO_2 + H_2O + CH_3OH \rightarrow 2C_5H_5N \cdot HI + C_5H_5N \cdot HI + C_5H_5N \cdot HSO_4CH_3$ (1)

$I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4$ -----------------(2)
(mol-equivalent of water = 18.016)

$I_2 + SO_2 + H_2O + CH_3OH = 2HI + HSO_4CH_3$ --(3)
(mol-equivalent of water = 9.008)

$3I_2 + 3SO_2 + 2H_2O + 4CH_3OH = 6HI + 2HSO4CH_3$ (CH3) $_2SO4$ --------------------------------------(4)
(mol-equivalent of water = 6.005)

Reaction (1) proceeds in a non-methanol reagent, and reaction (4) occurs in a reagent in which there is little pyridine (< 10% by volume). Only reaction (3) is typical for a Fischer reagent, which reacts quantitatively and selectively with water, to measure moisture content. it consists of iodine, sulfur dioxide, a base and a solvent, such as alcohol. Herein, a number of improvements were made to the Fisher water determination method. For example, a gel plug was used to prevent penetration of the reagent from the catholyte into the anolyte [16]. We also created a serial installation that allows titration of water with both Potentiometric and amperometric indications. The system is compatible with all known Fischer reagents (single-component and two-component; pyridine and non-pyridine; methanol and non-methanol). The method also compensates for the release of water as a result of adverse reactions in the Fischer reagent using a special digital function called "drift compensation" [17].

The water content in the sample is calculated by the formula:

$$\% \, H_2O = \frac{I. \, t. \, M.100}{96485,309.m}$$

I= generation current, A
T= time,sec
M=mole equivalent H_2O
m= mass of sample, gm

TABLE 2. Recommended sample size for coulometric titration (I=100 mA).

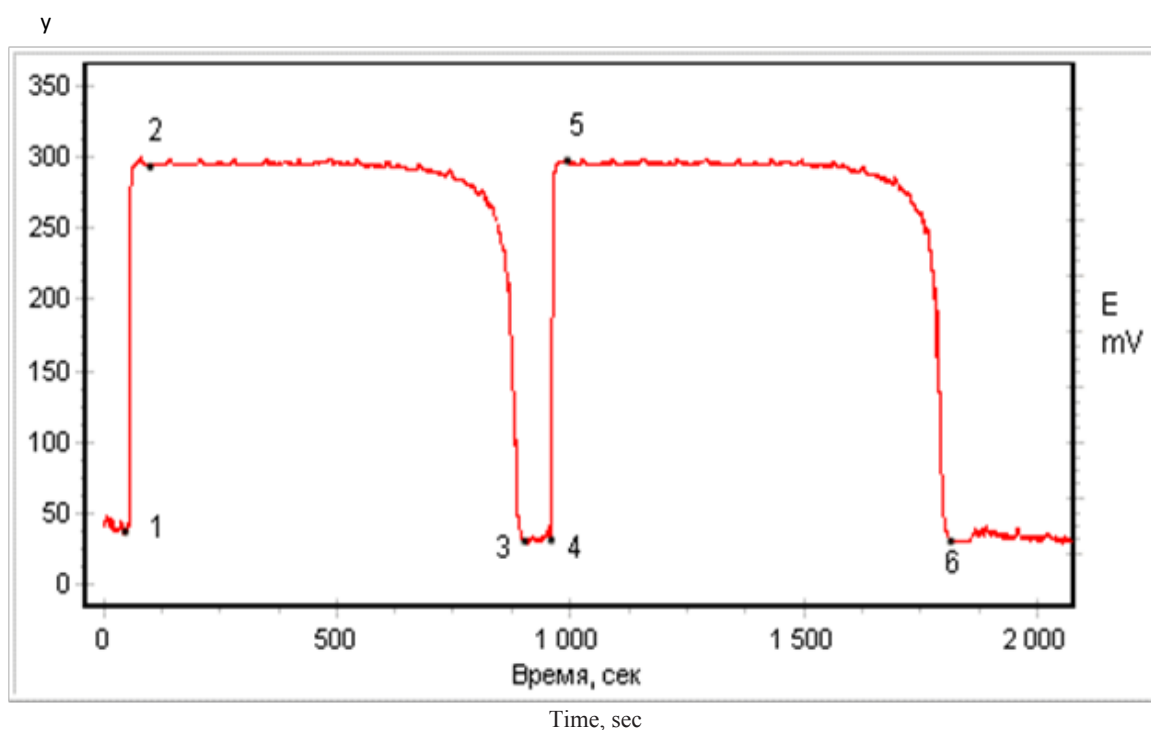| Water content,%	Sample size
10-100	10-1 mg (10-1 µL)
1-10	100-10 mg (100-10 µL)
0,1-1	1-0,1 g (1-0,1 ml)
0,01-0,1	10-1 g (10-1 ml)
0,001-0,01	10-1 g (10-1 ml)

Fig. 4. Titration curves for the determination of water in a refinery sludge.

Figure 4 shows the mechanism and reaction rate of the Karl-Fischer titration analysis. The reaction rate of the coulometric variant of the Karl-Fischer titration reaction(in that electrolytically generated triiodide is used as oxidant instead of iodine) has been measured in methyl alcohol. The reaction is first order in water, sulfur dioxide, and triiodide, respectively. The response time of the indicator electrode and the time of mixing of the triiodide formed to determine the maximum possible rate of potential decrease.

First order reaction rates to approximately 5 s -1 (i.e. about 50 mV potential decrease per second) were still reliable; at higher first order reaction rates too low values were always found for the determine water in oil crude [18].

As can be seen, the descending part of the E/mv curve is completely straight. Only when one of the concentrations of the constituents of the reagent was very small (or the buffering was insufficient)

the linearity of the E/mv curve was poor, but the initial slope was always well measurable.

Conclusion

The coulometric method described herein makes it possible to Measure a very small content of matter with high accuracy (0.1–0.05%) that exceeds the accuracy of many other methods. Coulometry is also characterized by high selectivity, which allowing Measurement of many substances in solution without prior chemical separation. The Coulometric analysis does not require any preliminary calibration of the measuring instruments by concentration or construction of calibration curves, and in this sense, coulometry should be considered an absolute method. This coulometric titration method is characterized by high accuracy, which allows direct Measurement of substances in solution at concentrations up to range 10^{-6} mol/l, which greatly exceeds the capabilities of other titrimetric methods. The method does not require preliminary preparation or standardization and storage of standard solutions. Furthermore, The use of coulometric titration for the determination of total sulfur in samples crude oil is demonstrated. Sulfur gases are evolved from the sample by igniting at 1050°C and are determined by automatic coulometric titration.

Acknowledgement

Conflict Interest Statement

There are no conflicts of interest to declare

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طريقة قياس جديدة لتحديد التركيب الكيميائي للمنتجات البترولية النفطية

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مركبات الكبريت العضوية هي مكونات طبيعية للنفط الخام. وجود هذه المركبات غير مرغوب فيه، لأنها تسبب تآكل المعدات وتلوث الغلاف الجوي أثناء الاحتراق. مركبات الكبريت تحطم المحفزات الباهظة الثمن وتطلق أكاسيد الكبريت في الغلاف الجوي عندما تحترق، مما يخلق مشاكل بيئية لذلك، هناك حاجة إلى طرق حديثة لاكتشاف وتحديد وقياس تركيزات الكبريت والماء والعناصر الأخرى في المنتجات البترولية. اقترح هذا العمل طريقة للتحليل الكمي للنفايات البترولية والنفطية، استناداً إلى طريقة قياس الكولومتري. توضح هذه المقالة الطرق لتحديد إجمالي كمية الكبريت في بقايا الزيوت وعدد الهيدروكربونات في الزيت اللزج. بالإضافة إلى ذلك تم قياس محتوى الماء من خلال قياس طريقة كارل فيشر في النفط الخام باستخدام طريقة الكولومتري، تم تطوير طريقة باستخدام أقطاب انتقائية أيونية وتطبيقها لتحديد تركيز الكبريت والماء في عينات الزيت الخام.