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Optimization of Sample Preparation Conditions for Ionochromatographic Determination of Chloride Ions That are Part of High-Molecular Organic Compounds of Oil

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Abstract. A procedure of sample preparation of oil samples for the determination of chloride ions, which are part of high-molecular organic compounds, has been developed. The procedure consists in the extraction of chloride ions from oil into the aqueous phase with a solution of sodium nitrate, followed by ionochromatographic detection. The work was performed on a high-performance LC-20 Prominence liquid chromatograph with LC Solution software (Shimadzu, Japan), equipped with a conductometric detector (CDD-10 Avp/10Asp), a 120×5 mm KanK-ASt14 μm separating column (GEOHI RAS, Russia) and a 200×6 mm SPS-SAC 50 suppression column μm (LLC PC «Aquilon», Russia). A carbonate buffer solution (2.5 mM Na₂CO₃ + 3.0 mM NaHCO₃) was used as an eluent. The volume of the injected sample is 100 μl. The eluent flow rate was 2.0 ml/min. The temperature of the column thermostat is 33 °C. Under these conditions, satisfactory separation of fluoride, chloride, nitrate, and sulfate ions is achieved, and hydrogen sulfide does not have ionic forms and does not manifest ionochromatographically. Using the method of full factorial experiment, the main parameters determining the efficiency of extraction of chloride ions from the organic phase were optimized: extraction of 1 mM with an aqueous solution of NaNO₃ at a temperature of 90 ± 2 °C, the volume ratio of oil and extractant 1:10, extraction time 20 min. The developed procedure of sample preparation has been tested on model solutions and real oil samples. In comparison with the known methods, the combination of extraction isolation of organic chlorides with ionochromatographic detection makes it possible to significantly simplify the procedure for determining the analyte due to the high selectivity of the method without loss in sensitivity and measurement accuracy.

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Оптимизация условий пробоподготовки для ионохроматографического определения хлорид-ионов, входящих в состав высокомолекулярных органических соединений нефти

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Аннотация. Разработан способ пробоподготовки образцов нефти для определения хлорид-ионов, входящих в состав высокомолекулярных органических соединений. Способ заключается в экстракционном выделении хлорид-ионов из нефти в водную фазу раствором нитрата натрия с их последующим ионохроматографическим детектированием. Работу выполняли на высокоэффективном жидкостном хроматографе LC-20 Prominence с программным обеспечением LC Solution (Shimadzu, Япония), укомплектованным кондуктометрическим детектором (CDD-10 Avp/10Asp), разделяющей колонкой 120×5 мм КанК-АСт14 мкм (ГЕОХИ РАН, Россия) и подавительной колонкой 200×6 мм СПС-SAC 50 мкм (ООО ПК «Аквилон», Россия). В качестве элюента применяли карбонатный буферный раствор (2,5 мМ Na₂CO₃ + 3,0 мМ NaHCO₃). Объем вводимой пробы 100 мкл. Скорость потока элюента составляла 2,0 мл/мин. Температура термостата колонки 33 °С. В данных условиях достигается удовлетворительное разделение фторид-, хлорид-, нитрат-, сульфат- ионов, а сероводород не имеет ионных форм и ионохроматографически не проявляется. С использованием метода полного факторного эксперимента оптимизированы основные параметры, определяющие эффективность извлечения хлорид-ионов из органической фазы: экстракция 1мМ водным раствором NaNO₃ при температуре 90±2 °С, объемное соотношение нефти и экстрагента 1:10, время экстрагирования 20 мин. Разработанный способ пробоподготовки апробирован на модельных растворах и реальных образцах нефти. По сравнению с известными методами сочетание экстракционного выделения органических хлоридов с ионохроматографическим детектированием позволяет существенно упростить процедуру определения аналита за счет высокой селективности метода без потери в чувствительности и точности измерений.

Ключевые слова: нефть, органические хлориды, ионная хроматография, определение.

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Introduction

The chemical composition of oil is very diverse and is a complex mixture of substances formed by basic (C, H, N, S, O) and impurity (10^{-7} – 10^{-2} %) elements [1]. Among the latter, the chlorine content can reach 10^{-2} % [2]. At the same time, chlorine is included in the composition of oil both in the form of inorganic chlorides (IC) and in the form of organochlorine compounds (COC) of various nature [3]. IC mainly sodium, magnesium and calcium enter the oil together with reservoir water. Their content can reach 2–3 g/dm³ and be 0.3–0.4 % by weight. The presence of IC causes corrosion of pipes. In addition, during oil refining, IC can form solid deposits, and under certain conditions, hydrogen chloride with high corrosive activity is isolated [4, 5]. Therefore, oil is thoroughly desalinated during preparation and transportation, and hydrogen chloride neutralizers – alkalis and amines – are added during distillation.

There are mainly two types of COC in crude oil: natural and chlorine-containing chemical reagents [6]. Natural COC are found in almost all oils and are mainly represented by organic salts and chlorine-containing ligands in metal complexes that are part of high-molecular components (asphaltenes). Their content depends on the nature of the oil and varies widely: from trace amounts to 97 mg/dm³ [7]. Natural COC also tend to turn into hydrogen chloride and ammonium chloride, which contributes to the failure of equipment at oil refineries [8]. Traditional technologies cannot provide complete removal of COC, therefore, for some oils their content is more than an order of magnitude higher than that for IC remaining in the oil after desalination.

Chlorine-containing chemical reagents (chloroform, carbon tetrachloride, dichloroethane and the like) are added to oil to increase oil recovery and remove paraffin deposits. In their pure form, these compounds are very stable, but during the distillation of oil they can also release hydrogen chloride [9].

Based on the above, it is obvious that analytical control of the content of chloride compounds in oil by known methods, as well as the development of new effective approaches to their determination remain urgent tasks. The purpose of this study is to optimize the sample preparation conditions for ionochromatographic determination of chloride ions that are part of high-molecular organic compounds of oil.

Experimental

The following materials were used in the work: oil samples; GSO 7262–96 composition of the chloride ion solution, GSO 7258–96 composition of the nitrate ion solution (JSC Ural Chemical Reagents Plant, Russia); carbonate, sodium bicarbonate (Sigma-Aldrich, USA); hexane, p.ch. for chromatography (JSC “ECOS-1”, Russia); nitric acid, p.ch. (LLC “Polychem”, Russia); deionized water (Yonglin installation, Korea).

The work was performed on a high-performance LC-20 Prominence liquid chromatograph with LC Solution software (Shimadzu, Japan), equipped with a conductometric detector (CDD-10

Avp/10Asp), a 120×5 mm KanK-ASt14 μm separating column (GEOHI RAS, Russia) [10] and a 200×6 mm ATP suppression column-SAC 50 μm (LLC PC «Aqilon», Russia). A carbonate buffer solution (2.5 mM Na_2CO_3 + 3.0 mM NaHCO_3) was used as an eluent. The volume of the injected sample is 100 μl . The eluent flow rate was 2.0 ml/min. The temperature of the column thermostat is 33 °C. The device was controlled and chromatograms were processed using the LCsolution program on a personal computer.

Chloride ions were extracted with an aqueous solution of 1 mM sodium nitrate. Extraction conditions were optimized by a full factorial experiment. To do this, 1 cm^3 of crude oil was placed in a dividing funnel, 10 cm^3 of heated extractant was poured, extraction was carried out for 20 min. Before chromatography to remove oil emulsion residues, the obtained aqueous extracts (5 cm^3) were placed in a 50 cm^3 separating funnel, 2,5 cm^3 hexane was added and extracted for 10–15 min. The aqueous phase was filtered through a PTFE 13 syringe filter (Millipore, Germany) and subjected to tests. In the methods of additives and «added-found» as a model high-molecular COC a solution of trioctylamine chloride ($(\text{C}_8\text{H}_{17})_3\text{NH}^+\text{Cl}^-$) in the dean was used.

The experiment was carried out at the Center for Collective Use “Science-intensive methods of research and analysis of new materials, nanomaterials and mineral raw materials” of the Federal State Autonomous Educational Institution of Higher Education “Siberian Federal University”.

Results and their discussion

In accordance with GOST R 52247–2021 «Oil. Methods for the determination of organochlorine compounds» the content of chloride ions in the COC of oil is determined by various methods [11]. Method A is diphenyl reduction followed by potentiometric titration. Method B – combustion in an inert gas and oxygen environment with subsequent microcoulometric titration. Method C is polychromatic wave dispersion X-ray fluorescence spectrometry using an internal standard. Method D – monochromatic wave- or energy-dispersive X-ray fluorescence spectrometry, as well as polychromatic energy-dispersive X-ray fluorescence spectrometry without using an internal standard. These methods make it possible to determine the mass fraction of organic chlorides in oil from 1 ppm. Along with the obvious advantages of the methods, it should be noted the complex and lengthy sample preparation, as well as the insufficient selectivity of analytical procedures. Thus, the initial stage of each method is the distillation of oil samples in order to isolate a fraction boiling to a temperature of 204 °C, and the removal of hydrogen sulfide in the resulting fraction by washing with a solution of potassium hydroxide. In addition, it is necessary to take into account the interfering effect of salts of hydrochloric acids (methods A, B), sulfur (method C, D), as well as matrix effects (method D).

Earlier [12] we published the results of studies on the ionochromatographic determination of IC in oil. The combination of deionized water extraction with ionochromatographic detection makes it possible to selectively determine inorganic chlorides with a detection limit of 0.01 mg/dm^3 . At the same time, satisfactory separation of fluoride, chloride, nitrate, and sulfate ions is achieved, and hydrogen sulfide does not manifest itself ionochromatographically under the conditions of a two-column ion chromatography with a carbonate-bicarbonate eluent [13]. The figure 1 shows a typical chromatogram of a model mixture of a number of anions obtained by us during the experiment.

According to the literature data [1] in asphaltenes of petroleum, COC are composed of nitrogen atoms with basic properties in which chlorine is in the ionic state. When these salts interact, in

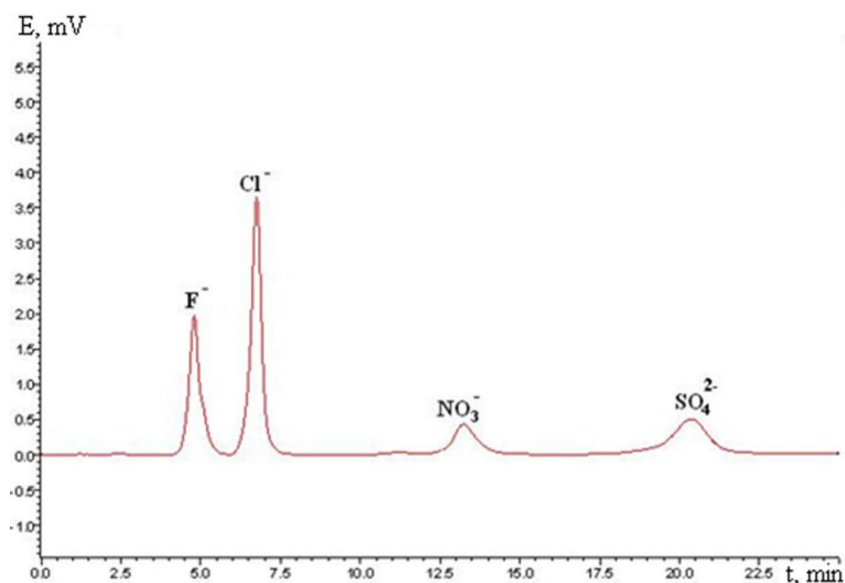
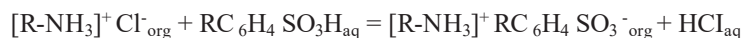
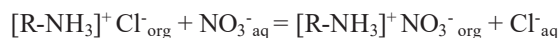


Fig. 1. Chromatogram of the model mixture of anions (mg/dm^3): F^- (1.5), Cl^- (4.0), NO_3^- (3.0), SO_4^{2-} (3.5), S^{2-} (5)

particular, high-molecular heterocyclic nitrogen-containing compounds with organic acid, the ion exchange displacement of chloride ions into the aqueous phase occurs:



There are known series of ion exchange of single-charged anions in similar systems in which the nitrate ion has a greater affinity for the organic matrix than the chloride ion [14]. Therefore, ion exchange extraction with an aqueous solution of nitrate ions is proposed for the effective extraction of chloride ions that are part of the high-molecular organic bases of oil. Using the example of a reaction with nitrogenous base chlorides [15], the basic heterogeneous equation can be represented as follows:



To optimize the extraction conditions, the method of a complete factorial experiment was used (Table 1) [16]. The following parameters are selected: x_1 – volume ratio of oil and extractant (1:5–1:10); x_2 – extraction time, min (10–20); x_3 – the temperature of the extractant, °C (60–90); y – the concentration of chloride ions, mg/dm^3 .

The maximum values of the variation parameters are chosen for reasons of expediency. Regression coefficients were calculated using the Yates method and known equations [17]. The significance of regression coefficients is estimated, a linear model is constructed and its adequacy is verified. The final regression equation looks like this:

$$y_u = 8,26 + 0,08x_1 + 0,03x_2 + 0,05x_3.$$

The adequacy of the regression equation was checked by the Fisher criterion. Based on the above calculations, it was concluded that the optimum was reached at $y_{\text{max}} = 8.41 \text{ mg}/\text{dm}^3$. Thus, optimal conditions for the extraction of chloride ions, which are part of the high-molecular organic bases of oil,

are achieved at a volume ratio of oil and extractant 1:10, the temperature of the extractant 90 °C and the extraction time 20 min.

The effectiveness of the proposed approach was evaluated on model solutions of trioctylamine chloride in decane by the «added-found» method (Table 2) and on real samples of prepared oil by the additive method (Table 3).

As can be seen from Tables 2, 3, satisfactory data for ionochromatographic determination of the chloride ion content have been obtained. The relative standard deviation in the determination of chloride ions in model solutions does not exceed 6 %, and the error of determination in oil by the additive method is 2 %.

Table 1. Matrix for planning a complete factorial experiment 2³

Experience No.	x ₁	x ₂	x ₃	y ₁	y ₂	y ₃	\bar{y}
1	–	–	–	8,10	8,09	8,11	8,10
2	+	–	–	8,25	8,26	8,24	8,25
3	–	+	–	8,17	8,16	8,17	8,17
4	+	+	–	8,33	8,33	8,32	8,33
5	–	–	+	8,22	8,21	8,23	8,22
6	+	–	+	8,37	8,38	8,36	8,37
7	–	+	+	8,23	8,22	8,23	8,23
8	+	+	+	8,41	8,41	8,40	8,41

Table 2. Results of ionochromatographic determination of chloride ions in model solutions (n=3, P=0.95)

Concentration of chloride ions, mg/dm ³		S	S _r , %
Added	Found		
1,5	1,6±0,3	0,1	6
9,5	10,0±1,2	0,5	5
35	36±3	1	3

Table 3. Results of ionochromatographic determination of chloride ion content in oil by addition method (n=3; P=0.95)

Experience No.	The value of the chloride ion additive, ppm	Found chloride ion quantity, ppm		The found quantity of the chloride ion additive, ppm	Δ, %
		Without additives	With an additive		
1	5,0	8,4 ±0,1	13,3±0,1	4,9	2
2	10,0	8,4 ±0,1	18,6±0,2	10,2	2
3	20,0	8,4 ±0,1	28,5±0,3	20,4	2

The developed approach has been tested in the analysis of oil samples from the fields of the Krasnoyarsk Territory. To ensure the correctness of the data, the quantity of IC in the oil samples was preliminarily determined before the tests according to the method [12]. Organic chlorides were determined by the difference between the contents of chloride ions during the extraction of oil samples with sodium nitrate solution and deionized water (Table 4).

Table 4. Results of ionochromatographic determination of chloride ions in oil samples (n=3, P=0.95)

Concentration of chloride ions in the extract, mg/dm ³		The quantity of chloride ions in oil, ppm		
extractant		Inorganic salts	Total chloride quantity	Organic salts (ion-exchange chlorine)
H ₂ O	1 mM NaNO ₃			
3,4±0,3	3,7±0,3	40±3	43±4	3
5,0±0,6	5,0±0,7	59±4	59±5	0
17,0±2,0	17,7±2,1	200±15	208±16	8
1,6±0,1	2,9±0,2	19±2	34±3	15
4,9±3,8	45,8±3,8	58±5	538±43	480
0,4±0,1	4,6±0,4	5±0,3	54±4	49

It follows from the data in Table 4 that the content of organic as well as inorganic chlorides in oil varies in a fairly wide range, which seems very important, for example, for screening samples in order to select the appropriate algorithm for preparing oil for transportation and subsequent processing.

Conclusion

In this paper, an approach for ionochromatographic determination of organic chlorides with preliminary extraction extraction of the latter with a solution of sodium nitrate is proposed and implemented on real oil samples. In comparison with the known methods [11], the combination of extraction isolation of organic chlorides with ionochromatographic detection makes it possible to significantly simplify the procedure for determining the analyte due to the high selectivity of the method without loss in sensitivity and measurement accuracy. However, it would not be entirely correct to assert that the nature of chlorine in the chemical composition of oil is limited only to high-molecular heterocyclic nitrogen-containing compounds. There is evidence of a variety of other condensed cyclic structures. To date, more than 5,000 halogen-containing organic compounds of natural origin have been described in the literature [18]. In addition, COC can undergo structural changes as a result of the influence of various factors.

References

- [1] Бадамшин А.Г., Носов В.В., Пресняков А.Ю., Волошин А.И., Невядовский Е.Ю., Докичев В.А. Генезис хлороорганических соединений в нефти и нефтепродуктах (обзор). *Нефтехимия*, 2021. 61(6), 776–787. [Badamshin A.G., Nosov V.V., Presnyakov A. Yu.,

Voloshin A. I., Nevyadovsky E. Yu., Dokichev V. A. The genesis of organochlorine compounds in oil and petroleum products (review). *Petrochemistry*, 2021. 61(6), 776–787. (In Russ.). DOI: 10.31857/S 0028242121060034.

[2] Эрих В.Н., Расина М.Г., Рудин М.Г. *Химия и технология нефти и газа*. Л.: Химия, 1985. 408 [Erich V. N., Rasina M. G., Rudin M. G. *Chemistry and technology of oil and gas*. L.: Chemistry, 1985. 408 (In Russ.)]

[3] Ma R., Zhu J. H., Wu B. C., Xue J. X. Distribution and hazards of organic chlorides in crude oil and its distillates. *Petroleum Refinery Engineering*, 2016. 46(4), 60–64.

[4] Heidersbach R. *Metallurgy and corrosion control in oil and gas production*. Hoboken: John Wiley & Sons, Inc., 2018. 368.

[5] Groysman A. *Corrosion problems and solutions in oil refining and petrochemical industry*. Springer International Publishing Switzerland, 2017. 356.

[6] Zhang X. J. Sources and distribution of chlorides in crude and the control measures. *Petroleum Refinery Engineering*, 2004. 34(2), 14–16.

[7] Новиков Е.А. Определение хлора в нефти. Обзор аналитических методов. *Мир нефтенпродуктов*, 2019. (7), 39–50. [Novikov E. A. Determination of chlorine in petroleum. Overview of analytical methods. *The world of petroleum products*, 2019. (7), 39–50. (In Russ.)]

[8] Xiaohui L., Bencheng W., Jianhua Z. Hazards of organic chloride to petroleum processing in Chinese refineries and industrial countermeasures. *Progress Petrochem Sci.* 2018. 2(3), 204–207. PPS.000539. DOI: 10.31031/PPS.2018.02.000539.

[9] Носов В.В., Пресняков А.Ю., Бадамшин А.Г., Невядовский Е.Ю., Волошин А.И., Докичев В.А. Хлорорганические соединения в нефти: проблемы и решения. *Нефтяное хозяйство*, 2021. (4), 110–113. [Nosov V. V., Presnyakov A. Yu., Badamshin A. G., Nevyadovsky E. Yu., Voloshin A. I., Dokichev V. A. Organochlorine compounds in oil: problems and solutions. *Oil industry*, 2021. (4), 110–113. (In Russ.)]. DOI: 10.24887/0028–2448–2021–4–110–113.

[10] Долгоносов А.М. Сорбенты КанК для ионных хроматографов. *Наука – производству*, 2001. (1), 52–56 [Dolgonosov A. M. KanK sorbents for ion chromatographs. *Science – Production*, 2001. (1), 52–56. (In Russ.)]

[11] ГОСТ Р 52247–2021. Нефть. Методы определения хлорорганических соединений. [GOST R 52247–2021. Oil. Methods for the determination of organochlorine compounds. (In Russ.)]

[12] Полосухина М.А., Калякина О.П., Качин С.В. Оптимизация условий пробоподготовки нефти для определения хлорид-ионов методом ионной хроматографии. *Международный журнал прикладных и фундаментальных исследований*, 2021. (10), 120–124. [Polosukhina M. A., Kalyakina O. P., Kachin S. V. Optimization of oil sample preparation conditions for the determination of chloride ions by ion chromatography. *International Journal of Applied and Fundamental Research*, 2021. (10), 120–124. (In Russ.)]

[13] Долгоносов А.М., Рудаков О.Б., Суровцев И.С., Прудковский А.Г. *Колоночная аналитическая хроматография как объект математического моделирования*. Воронеж, 2013. 400 [Dolgonosov A. M., Rudakov O. B., Surovtsev I. S., Prudkovsky A. G. *Column analytical chromatography as an object of mathematical modeling*. Voronezh, 2013. 400 (In Russ.)]

[14] Нестеров Ю.В. *Иониты и ионообмен. Сорбционная технология при добыче урана и других металлов методом подземного выщелачивания*. М.: 2007, 480 [Nesterov Yu. V. *Ionites and ion exchange. Sorption technology in the extraction of uranium and other metals by leaching*. M.: 2007, 480

and ion exchange. *Sorption technology in the extraction of uranium and other metals by the method of surface leaching*. Moscow, 2007, 480 (In Russ.)]

[15] Камьянов В.Ф., Аксенов В.С., Титов В.И. *Гетероатомные компоненты нефтей*. Новосибирск: Наука, 1983. 236 [Kamyanov V.F., Aksenov V.S., Titov V.I. *Heteroatomic components of oils*. Novosibirsk: Nauka, 1983. 236 (In Russ.)]

[16] Сауткин С.Н. *Планирование эксперимента в химии и химической технологии*. Л.: Химия, 1975. 135 [Sautkin S.N. *Experiment planning in chemistry and chemical technology*. L.: Chemistry, 236 (In Russ.)]

[17] Сафронова Н.А., Лагуткина Е.В., Белов В.М., Иванкова В.П. Результирующий полный факторный эксперимент при хлорметилировании гидролизованного лигнина. *Химия растительного сырья*, 1997. (3), 59–60. [Safronova N.A., Lagutkina E.V., Belov V.M., Ivankova V.P. The resulting complete factorial experiment in the chloromethylation of hydrolyzed lignin. *Chemistry of plant raw materials*, 1997. (3), 59–60 (In Russ.)]

[18] Gribble G. W. Newly discovered naturally occurring organohalogens. *Arkivoc*, 2018. Part I. 372–410. DOI: 10.24820/ark.5550190.p010.610.