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Determination of Oil Products in Waste and Natural Waters Using Tetrachloromethane

Vasiliy Trokhin, Arkadiy Bessarabov*, Denis Sevastyanov, Lyubov' Trynkina, Tatiana Stepanova, Andrey Vendilo

Science centre "Low-tonnage chemistry" (SC "LTC"), Krasnobogatyrskaya st. 42, Moscow, 107564, Russia
E-mail: bessarabov@nc-mtc.ru

At present water pollution by oil products is a widespread phenomenon. Industrial sewage, oil escape during transportation, waste waters from refueling stations and motor transport lead to pollution of surface waters. Oil production results in substantial pollution of natural waters. In addition, natural waters are contaminated by filtration of oil products from ground surface. Topicality of detection of oil products continuously increases, because crude oil and oil products are the most abundant pollutants of anthropogenic origin. Large-scale environmental pollution occurs by both crude oil and products of oil refining (solvents, gasolines, lubricating oils, bitumen, and so on) during production, transportation and usage of such products.
Procedure for determination of oil products in water using tetrachloromethane includes three successive stages (operations): isolation of emulsified and dissolved oil components from water by extraction with tetrachloromethane; chromatographic separation of oil products from accompanying organic compounds of other classes by means of a column filled with aluminum oxide; quantitative determination of mass concentration of oil products on the basis of absorption intensity of C-H bonds at the infrared region using concentration meter. Modern analytical equipment allows determining concentration of oil products up to 0.0005 mg/l, while maximum permissible concentration of oil products is 0.05 mg/L in accordance with Russian Sanitary regulations and standards.

1. Analytical monitoring of tetrachloromethane

We developed the system of analytical monitoring for tetrachloromethane of 9 qualifications (see Figure 1) based on the modern CALS (Continuous Acquisition and Life cycle Support) concept (Saaksvuori and Immonen, 2010), which is used in the most perspective and innovative areas of science and industry (Bessarabov et al., 2002; Bessarabov et al., 2004; Bessarabov et al., 2012a; Bessarabov et al., 2012b). The system of analytical monitoring, also called as the system for computer-aided quality monitoring (Bessarabov and Zhdanovich, 2005), includes 3 hierarchy information levels: substance under study, quality indicators, and methods of analysis (Treger et al, 1984). The upper level of the system for computer-aided quality monitoring contains qualifications of CCl_4 ("Substance under study") combined into 4 categories (grades): No. 1 "Ultra-pure"; No. 2 "Chemically pure"; No. 3 "Analytical reagent"; No. 4 "Pure". The various quality indicators for tetrachloromethane of the above-mentioned grades, methods of analysis and analytical instruments (Kutseva et al., 2005) were entered into the categories of the created CALS-project. Determination of impurities in tetrachloromethane using NMR-, IR spectroscopy and gas-liquid chromatography was examined.
Category No. 1 contains two qualifications of "ultra-pure" grade: "ultra-pure 18-4" and "ultra-pure OP-3". Tetrachloromethane of "ultra-pure 18-4" qualification is designed for cleaning and degreasing of electronic components in electronics and radio engineering. Category No. 2 "Chemically pure" contains 5 qualifications of tetrachloromethane: «Chemically pure without chlorine and sulfur", "Chemically pure", "Chemically pure for UV spectroscopy", "Chemically pure for extraction from aqueous media", and "Chemically pure for chromatography". "Chemically pure without chlorine and sulfur" qualification is used in

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analytical chemistry of crude oil as solvent for analysis of oil products for chlorides and sulfur content. Categories No. 3 (“Analytical reagent”) and No. 4 (“Pure”) contain only one qualification: “Analytical reagent” and “Pure”, respectively. Tetrachloromethane of “Analytical reagent” qualification is used in scientific research, for cleaning and preparation of laboratory instruments, cells and glassware.

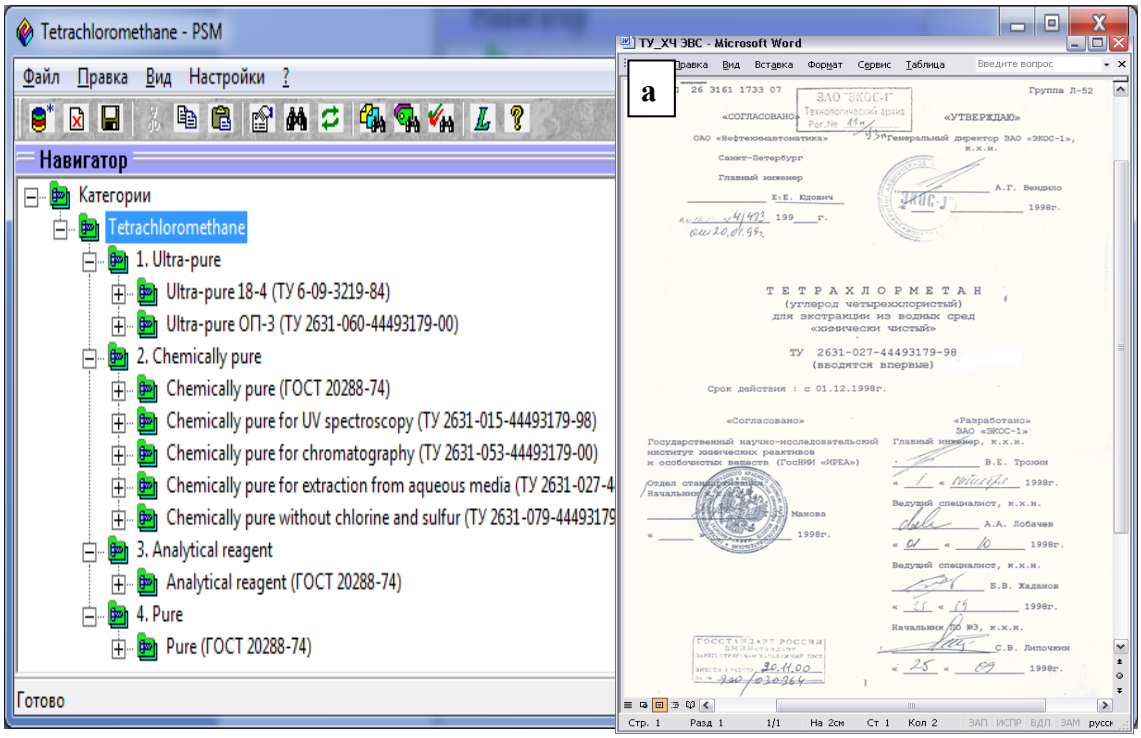

Figure 1. The element of the CALS-project. Substance under study: tetrachloromethane (a – the title page of technical specifications for “Chemically pure for extraction from aqueous media” CCl4)

One of the main applications of the system for computer-aided quality monitoring is determination of oil products in waste and natural waters using tetrachloromethane of “Chemically pure for extraction from aqueous media” qualification (Bessarabov et al., 2007). Procedure for determination of oil products in water using tetrachloromethane includes three successive stages (operations): isolation of emulsified and dissolved oil components from water by extraction with tetrachloromethane; chromatographic separation of oil products from accompanying organic compounds of other classes by means of a column filled with aluminum oxide; quantitative determination of mass concentration of oil products on the basis of absorption intensity of C-H bonds at the infrared region using concentration meter. Modern analytical equipment allows determining concentration of oil products up to 0.0005 mg/L, while maximum permissible concentration of oil products is 0.05 mg/l in accordance with Russian Sanitary regulations and standards.

At present water pollution by oil products is a widespread phenomenon (Vitenberg et al., 2011). Industrial sewage, oil escape during transportation, waste waters from refueling stations and motor transport lead to pollution of surface waters (Singovszka and Balintova, 2012). Oil production results in substantial pollution of natural waters. In addition, natural waters are contaminated by filtration of oil products from ground surface. Topicality of detection of oil products continuously increases, because crude oil and oil products are the most abundant pollutants of anthropogenic origin. Large-scale environmental pollution occurs by both crude oil and products of oil refining (solvents, gasolines, lubricating oils, bitumen, and so on) during production, transportation and usage of such products.

Purity of tetrachloromethane plays a crucial role in the two last stages of the described procedure for determination of oil products in water, since qualitative composition and concentration of impurities in CCl_4 (used as an extractant) have a great impact on IR spectroscopy and gas-liquid chromatography: impurities, which are present in tetrachloromethane, may impair optical transmittance of the reagent in the wavelength range used in concentration meters, and may pollute a chromatographic column. In this regard, manufacturers are now being faced with serious problems concerning tetrachloromethane production and purification.

Impurity composition for commercial-grade tetrachloromethane (raw material for production of chemicals) is dictated by its production process. Below are listed the industrial-scale methods of tetrachloromethane production: chlorination of carbon disulfide, chlorination of methane, exhaustive chlorination of C_1-C_8 hydrocarbons and their derivatives, high-temperature chlorinolysis of any hydrocarbons and their chlorinated derivatives at a pressure up to 20.2 MPa (Treger et al., 1984). At present tetrachloromethane is produced mainly by methane chlorination and high-temperature chlorinolysis of hydrocarbons and their derivatives.

Impurities, exerting considerable influence on quality of the product, are the following: industrial lubricating oils and greases used in production and preparation of transporting containers; substances formed as a result of destruction of sealing and gasket materials by the action of tetrachloromethane. This class of impurities was removed by means of selection of appropriate containers used for CCl_4 transportation and storage.

The second hierarchy level ("Quality indicators") defines structuring and grouping for each substance in accordance with the quality requirements (see Figure 2).

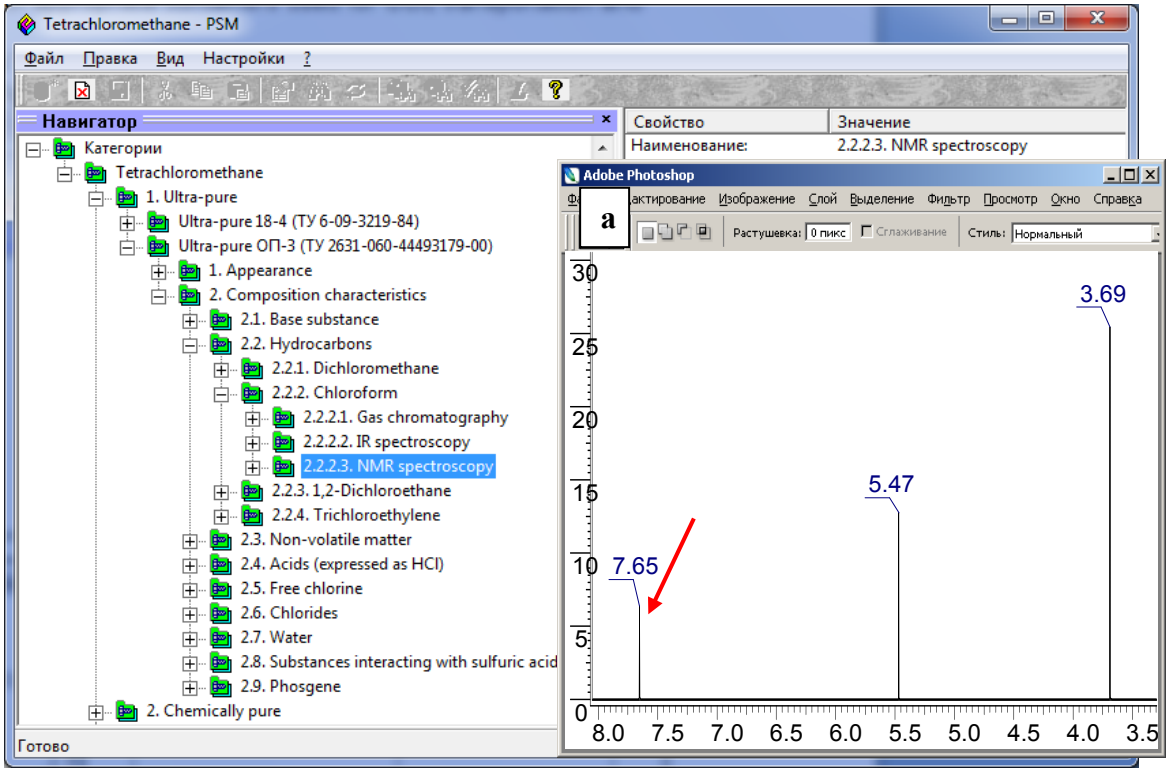

Figure 2. The element of the CALS-project. NMR spectroscopy (a – NMR absorption spectrum for tetrachloromethane containing chloroform and dichloromethane as impurities)

In each specific case requirements to product quality and necessity to determine quality indicators are defined by peculiarities of product application. For example, tetrachloromethane of "Chemically pure for extraction from aqueous media" qualification is used for IR spectroscopy. Tetrachloromethane of "Ultra-pure OP-3" qualification is used for NMR spectroscopy. Quality indicators for tetrachloromethane of "Ultra-pure OP-3" qualification are shown within the CALS-project in Figure 2. Subcategory No. 1 "Appearance" contains information about the test results for this indicator, subcategory No. 2 "Composition characteristics" consists of 9 second-level subcategories: 2.1 – "Base substance", 2.2 – "Hydrocarbons", 2.3 – "Non-volatile matter", 2.4 – "Acids (expressed as HCl)", 2.5 – "Free chlorine", 2.6 – "Chlorides", 2.7 – "Water", 2.8 – "Substances interacting with sulfuric acid", and 2.9 – "Phosgene".

The third hierarchy level contains methods of analysis of the corresponding quality indicators with indication of applicable state standard, branch standard and technical specifications. Each subcategory contains the test results for the corresponding quality indicator. For example, second-level subcategory 2.2 "Hydrocarbons" includes 4 third-level subcategories related to the following impurities: dichloromethane (subcategory 2.2.1), chloroform (2.2.2), 1,2-dichloroethane (2.2.3), and trichloroethylene (2.2.4). Methods for determination of the above-mentioned hydrocarbons are also listed. In case of chloroform the following

methods are used: gas chromatography (subcategory 2.2.2.1), IR spectroscopy (2.2.2.2), and NMR spectroscopy (2.2.2.3) (Figure 2-a).

2. Complex analysis of the oil products in water areas

Superposition of results of tetrachloromethane analysis by different methods is of considerable interest. In spectroscopy tetrachloromethane is used for extraction of oil products from aqueous media with subsequent qualitative determination of oil products using uasCH band (with maximum at 2925 cm^{-1}).
At present, to monitor dissolved and emulsified oil products in waste waters of industrial enterprises, the technique based on extraction of impurities from water with CCl_4 and their subsequent determination by means of infrared photometers of AN-1,2,3 types is used (Figure 3).

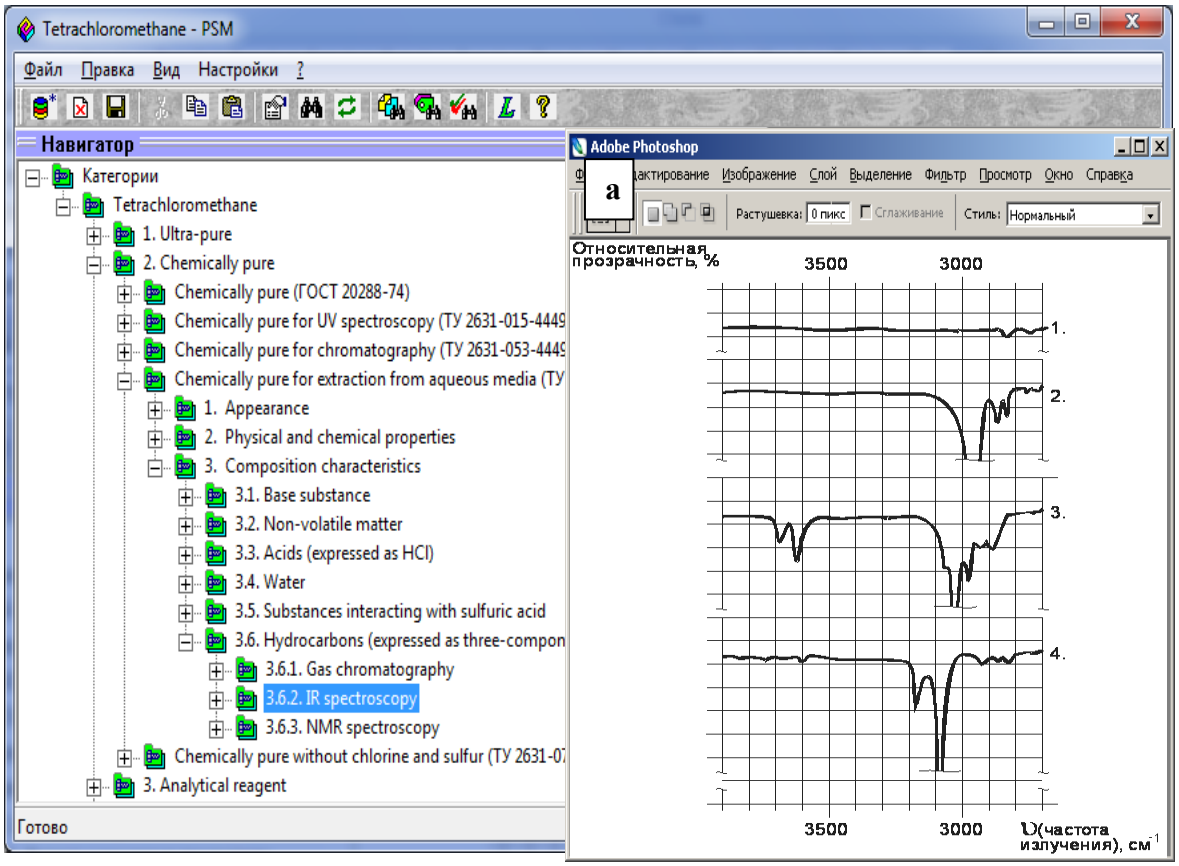

Figure 3. The element of the CALS-project. IR spectroscopy (a - absorption spectra for tetrachloromethane (1) containing 1,2-dichloroethane (2), chloroform (3) and trichloroethylene (4) as impurities).

Operating wavelength of infrared photometer AN-2 is 3.48 nm (2925 cm^{-1}), with adsorption peaks υ(acc.) of C-H bonds of aliphatic and aromatic hydrocarbons being located near the operating wavelength. Determination of gross-concentrations of such hydrocarbons is the main task during detection of oil products in water. Studies were undertaken to identify organochlorine impurity having the most prominent effect on infrared spectrum near 2925 cm^{-1}.
According to literature data, absorption spectra of 1,2-dichloroethane, chloroform and trichloroethylene lie in the range 2950-2970 cm^{-1}, 3010 cm^{-1}, and 3080-3100 cm^{-1}, respectively (Pretsch et al., 2006). It was found that 1,2-dichloroehtane had the greatest influence on spectrum due to the presence of many C-H bonds. This leads to substantial adsorption near 2925 cm^{-1}, if impurity content exceeds 0.02 % wt. Other impurities are not superimposed in the range of interest and have no influence on analytical purity (Figure 3-a).
Detection of impurities in tetrachloromethane using gas-liquid chromatography. Table 1 lists comparative data on efficiency of separation of impurities in tetrachloromethane by means of gas-liquid chromatography using different stationary phases and at different temperatures of columns and evaporator.

Table 1: Parameters of chromatographic analysis of impurities in tetrachloromethane

Desig-nation	Characteristics	Column temperature, °C	Evaporator temperature, °C	Selectivity of impurity separation with respect to base substance				
				TCE	PCE+TCM		DCE	DCM
A	Polisorb 1	170	170	1.31	PCE 2.79	TCM 0.81	1.18	0.44
B	Apiezon L	80	150	1.33	-		0.76	-
C	Tricresyl phosphate	90	170	1.68	PCE 2.95	TCM 1.35	1.82	0.68
D	PEG-300	60	150	1.93	PCE 2.15	TCM 2.4	3.13	1.33
E	PEG-300	50	150	2.27	2.72	2.98	-	1.46
F	PEG-1000	60	170	2.09	2.57		3.55	1.35
G	PEG-1000	70	170	1.98	2.41		3.22	1.30
H	PEG-1000	80	170	1.88	2.29		2.95	1.26

Polyethylene glycol (PEG-1000, PEG-300), Apiezon L, tricresyl phosphate and Polisorb 1 were used as stationary phases. Columns from stainless steel of 3 mm in diameter and 3-4 m in length were utilized.

Velocity ratio of the components of the analyzed mixture in a chromatographic column (α_k) was used as a measure of selectivity: $\alpha_k = t_{m2}/t_{m1}$, where t_{m2} is retention time of an impurity, and t_{m1} is retention time of the base substance (tetrachloromethane).

Selectivity, defined by the ability of a chromatographic system (sorbent and mobile phase) to separate the specific pair of compounds, depends on the nature of the liquid phase, percentage of coating onto the solid support, conditions of analysis, and packing density of the sorbent in a column. Knowledge of α allows optimizing selection of chromatographic conditions depending upon the problem to be solved.

Figure 4 presents schematic view of the obtained chromatograms for separation of mixtures containing tetrachloromethane (3) and the following impurities: dichloromethane (1), trichloromethane (2), dichloroethane (4), trichloroethylene (5), and perchloroethylene (6).

It was found using comparative analysis that the best resolution occurred at the column of 3.0×4000 mm in size; the stationary phase is 10 % PEG-1000, the support is dinokhrom H with particle size 0.25-0.315 mm, temperature of the column thermostat is 60 °C (Figure 4).

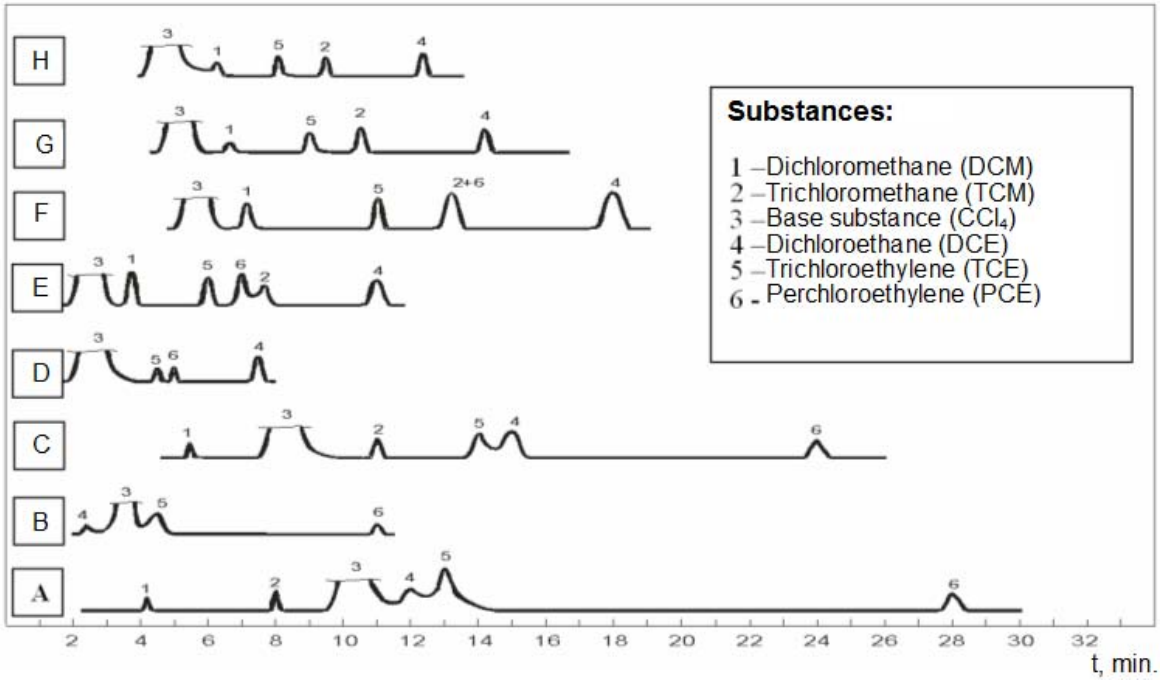

Figure 4. Chromatograms for separation of mixtures at different columns

Statistical analysis of gas-liquid chromatography and IR spectroscopy data for tetrachloromethane were used to study dependence of hydrocarbon concentrations (mg/l), determined using concentration meter An-2, on concentration of 1,2-dichoroethane (% wt.) in tetrachloromethane. Analysis of the obtained dependence revealed its linear character in the studied range of concentrations (from 0 to 0.16 % wt. dichloroethane). In addition, it was found that content of hydrocarbons conformed to technical specifications for tetrachloromethane of "Chemically pure for extraction from aqueous media" qualification, provided that 1,2-dichloroethane concentrations < 0.02 % wt.

The obtained result confirms the conclusion that the limiting impurity having the main influence on quality of tetrachloromethane is 1,2-dichloroethane. Based on this result, it is better to use concentration meter An-2 to determine 1,2-dichoroethane content (it takes 1-2 minutes as compared to 15-20 min in case of gas-liquid chromatography without sample preparation). Also it is possible to design automatic analyzer of 1,2-dichloroethane in the purification unit using a flow-through cell.

3. Conclusions

The developed system for computer-aided analytical monitoring makes it possible to optimize determination of oil products in natural and waste waters due to concentration of the necessary information on chemicals and methods of analysis, to implement the comprehensive approach and select the most reasonable way of analytical research.

Input, editing and analysis of information on quality indicators of tetrachloromethane and monitoring methods (NMR spectroscopy, IR spectroscopy and gas-liquid chromatography) were made using PDM STEP Suite Enterprise Edition (PSS-EE) system with the license (APL-3451631-01) obtained. Application of the CALS-standard (ISO 10303) for development of information system of analytical monitoring allows increasing quality and operability of analytical research. Eventually, the selected information technology allows developing effective system of analytical monitoring (conforming international standards) for such important chemical substance as tetrachloromethane.

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