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Determination of Oil Products in Waste and Natural Waters Using Tetrachloromethane

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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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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).

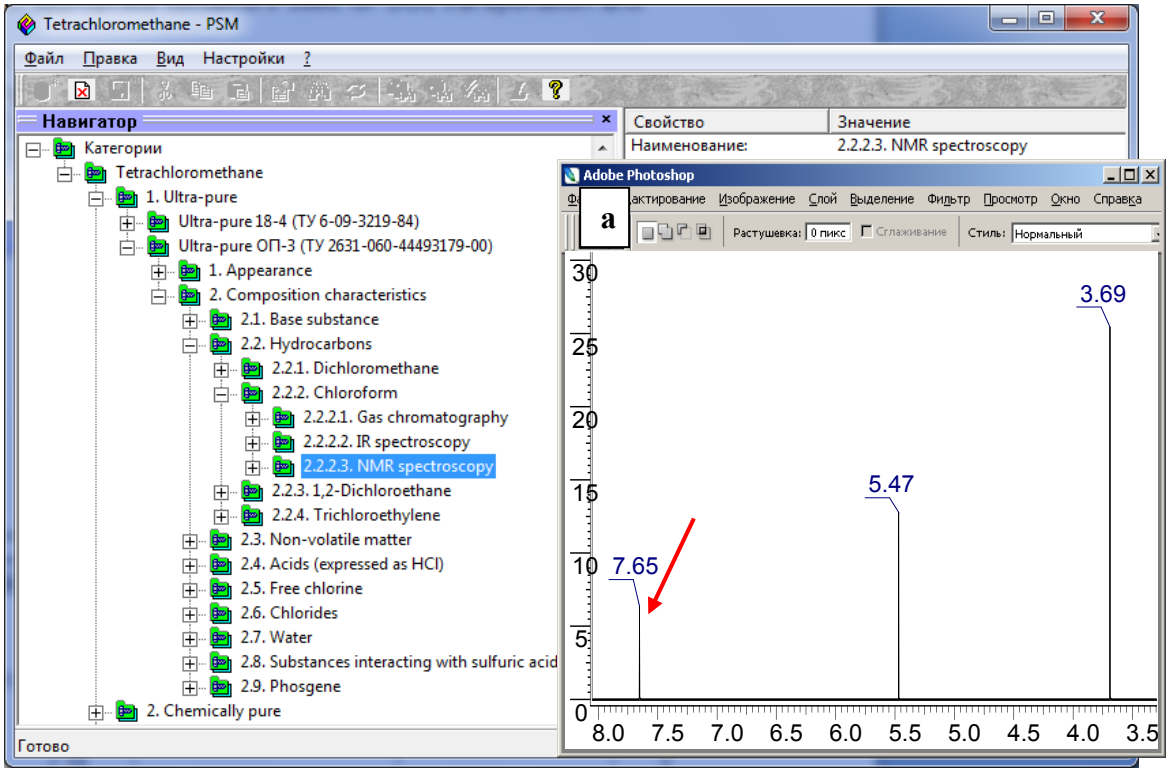

Figure 2. The element of the CALS-project. NMR spectroscopy (a – NMR absorption spectrum for tetrachloromethane containing chloroform and dichloromethane as impurities)

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

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).

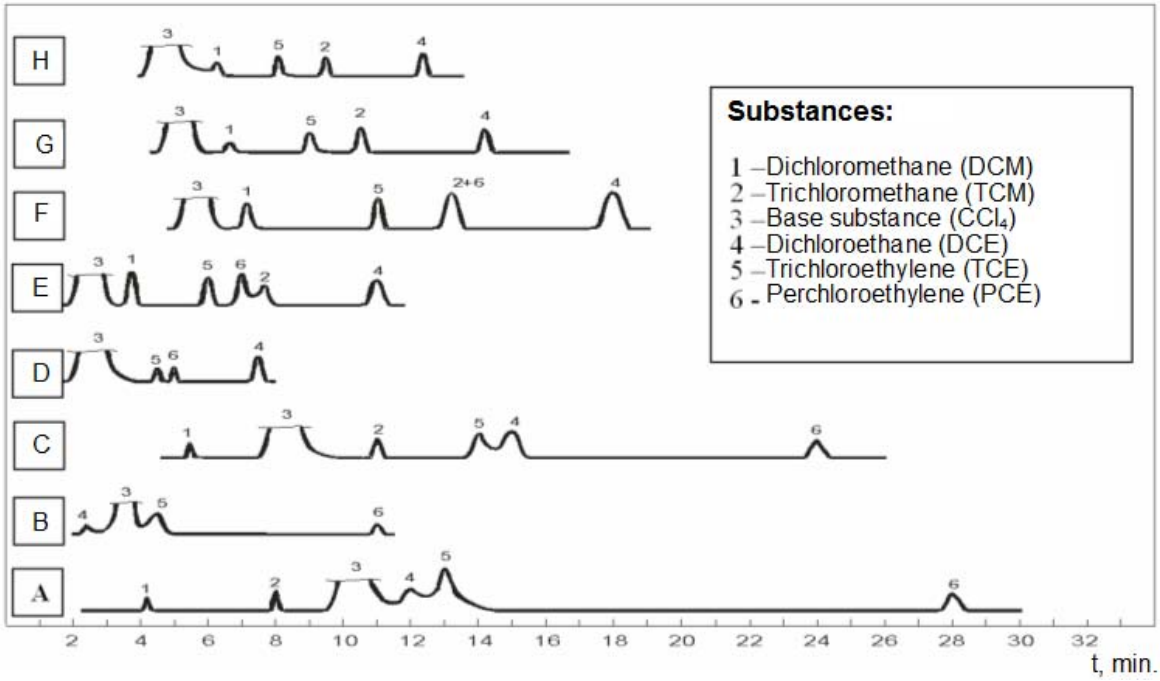

Figure 4. Chromatograms for separation of mixtures at different columns