IV. ANALYSIS OF CHEMICAL CONTAMINANTS

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Physicochemical analysis of organic toxic substances in natural waters

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One of the most important problems in preserving the environment is the identification and quantitative determination of the contaminating substances passing into it. Upwards of 1000 organic compounds are included in the list of priority contaminants of the biosphere.[1] The main organic contaminating substances of natural waters are recognised to be phenols, lignins, pesticides and petrochemicals.

Investigations have been carried out by us recently with the aim of developing procedures for the qualitative and quantitative analysis of the various classes of contaminating substances, primarily hydrocarbons and phenols, using physicochemical methods such as capillary gas chromatography (CGC), gas chromatography-mass spectrometry (GCMS) and nuclear magnetic resonance spectroscopy (NMR).

Petrochemical hydrocarbons are some of the main and stable contaminants of aqueous media. As a result of human activity more than a million tons of petrochemicals pass into the oceans of the world every year, 90% entering with fresh water.[2] Such contamination of the oceans leads to a disturbance of the ecological balance, accumulation of petrochemicals in aqueous organisms and correspondingly in man.[3]

CGC and GCMS are universal methods of analysis of oil and petrochemicals in the environment. This is linked with the ability of chromatographic methods to resolve complex mixtures and with the high sensitivity of chromatographic and mass spectrometric detectors.

CGC was used for the determination of contamination by paraffin hydrocarbons of the western waters of the Black Sea.[4] Water was sampled at 25 points of the coastal waters to the west of longitude 32° E in April 1981. Samples of water were extracted with chloroform and the paraffin hydrocarbon fraction was separated from the extracts. The concentration of n-alkanes containing from 14 to 44 carbon atoms was determined by GLC.

In the region investigated the overall concentration of n-alkanes varied from 2 to 400 μg litre^{-1}. The coastal zone and also all the navigable region was characterised by an increased content of hydrocarbons (see Fig. 1). This may be explained by contamination of the Black Sea both by carry down from rivers and by means of transport.

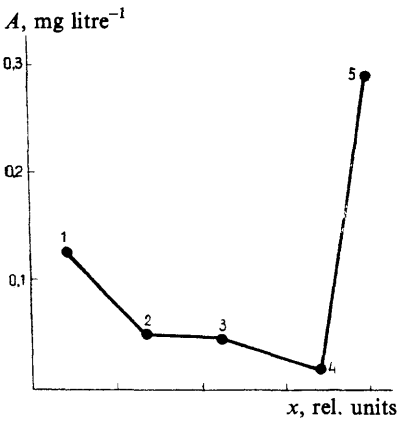


Figure 1. Dependence of the total content of n-alkanes (A) in water from the Black Sea on distance (x) from the coast: *1*, station 36; *2*, station 35; *3*, station 34; *4*, station 33; *5*, station 31.

An important question linked with contamination of the world's oceans by petrochemicals is the solution of the arbitrary problem of the search for the culprits of petroleum contamination.

A complex approach to the solution of this problem was used by us in several cases when determining culprits for the catastrophic oil spills in the Baltic Sea. In this case CGC was used for determining the ratios of quantities of isoprenoid and normal hydrocarbons Ph/C_n and Pr/Ph, where $n > 18$, Ph is phytane and Pr is pristane, from which the culprits of the spills were identified.

It was established previously,[5-7] that NMR spectroscopy enables analysis of both crude petroleum and its refined products including heavy fractions not yielding to chromatography. This method is used together with other physicochemical methods for the estimation of structure-group parameters of petroleum. The main parameters determined by NMR are the relative content of aromatic protons H_a (contribution of the integrated intensity of signals for aromatic protons in the ^1H NMR spectrum to the total integrated signal intensity) and the relative content of aromatic hydrocarbons C_a (contribution of the integrated intensity of signals for aromatic carbons in the ^{13}C NMR spectrum to the total integrated signal intensity). It was shown that it was necessary to use a relaxant such as chromium(III) acetylacetonate for the quantitive determination of the C_a parameter and a method for decoupling the spin-spin interaction of ^{13}C nuclei with protons. The decoupling unit was switched on during the time for sensing the impulse of the radiofrequency field and was switched off during the time for sensing the free induction signal. This led to the quenching of the nuclear Overhauser effect.

Analysis of specimens of petroleum spills showed that depending on the weathering of the petrochemicals, H_a may vary several fold while the C_a parameter was practically unchanged. In addition data from the analysis of numerous oilfields of the Soviet Union showed[7] that the range of change of C_a was wider than that of H_a and was 9–23%. Consequently the C_a parameter, together with the overall shape of the ^{13}C NMR spectrum, which enabled determination of the oil type, paraffinic or napthenic, was used to determine the source of origin of the oil spill into the sea.

Table 1. Results of analyses of contamination of the Baltic Sea by hydrocarbons.

Parameter	Sample				
	Control oil		Oil I, weathered	Contamination samples taken from the sea	
	I	II		I	II
H_a, %	4.0	0	2.2	2.3	1.5
C_a, %	18	14	20	18	19
Pr/C_{17}	0.59	0.98	0.50	0.49	0.52
Ph/C_{18}	0.78	0.56	0.72	0.71	0.72
Pr/Ph	0.75	1.75	0.70	0.69	0.72

Data shown in Table 1 of CGC and NMR which were used for determining the culprit for a catastrophic oil spill in the Baltic Sea. Samples presented for analysis were from two assumed sources of the spill (oils I and II), an oil sample subjected to 40 days weathering under laboratory conditions (oil I, weathered) and samples of contamination taken from the sea (I and II). NMR data and the ratios of isoprenoid hydrocarbons Pr/Ph showed that oil from the first source had spilled into the sea.

The procedure for determining the culprit for the contamination by GCMS was based on the detection of aromatic compounds of the homologous series benzene, naphthalene, anthracene and phenanthrene. Since polynuclear aromatic hydrocarbons are less subject to weathering and biodegradation in water in comparison with aliphatic hydrocarbons for example[8,9] the probability of correctly identifying the culprit of a spill by detection of these compounds is high. It appeared possible to analyse petrochemicals which had been in the sea for several days (their composition was very different from that initially).

In the case of water with little contamination, i.e. when the sensitivity of the gas chromatograph-mass spectrometer was inadequate to carry out an analysis in the field scanning mode, monitoring of definite ions from aromatic hydrocarbons of the series indicated was used. To detect homologues of benzene the instrument was adjusted to record ions of mass m/z 77, 91 and 105, of naphthalene 127, 141 and 155 and of anthracene and phenanthrene 177, 191 and 205. Such a procedure enabled the sensitivity of determining aromatic hydrocarbons to be increase 100–1000 times. The culprit of the contamination was determined fairly simply from the chromatogram drawn from the current of the indicated ions.

Table 2. Content of some organic contaminants in test samples of snow and water in Kemerovo.

Compound	Concentration ($\mu g\ litre^{-1}$)	
	snow	water
Hexadecane	112.0	2.9
Pentadecane	151.0	2.8
Octadecane	75.4	3.9
Nonadecane	70.0	9.0
Tricosane	98.0	4.4
Octacosane	98.0	2.0
Nonacosane	279.0	traces (<0.5)
Triacontane	70.5	traces (<0.5)
Untriacontane	184.5	—
Dotriacontane	112.0	—
Tritriacontane	80.0	—
Tetratriacontane	37.1	—
Naphthalene	5.7	3.0
Methylnaphthalenes	0.4	—
Acenaphthene	10.0	traces (<0.1)
Anthracene	1.5	traces (<0.1)
Pyrene	traces	traces
Dibenz[*a*,*c*]anthracene	8.1	0.5
Phenol	0.7	traces (<0.5)
Dimethylphenols	traces (<0.5)	0.9
4-Chlorophenol	—	1.0
4-Chloro-*m*-cresol	—	4.8
2,6-Di-t-butylphenol	—	
4-Methylphenol	3.0	
Oct-2-ene (isomers)	—	112.0
t-Butylmethylcarbinol	—	10.1
iso-Butylmethyl carbinol	—	13.7
Bis(2-chloroethyl) ether	—	65.0
Bis(2-chloropropyl) ether	—	63.1
Bis(2-chloroisopropyl) ether	—	30.0

Contamination of surface waters may also occur from the atmosphere since[10] on going from alkanes to a polynuclear aromatic hydrocarbon the size of the contribution of this contamination to the total contamination of water increases from 1–2 to 25%. Gas chromatographic analysis of samples of snow taken in March 1988 near Kemerovo showed that alkanes and aromatic hydrocarbons

were the principal organic contaminants of snow. For example, the content of individual n-alkanes was 100–200 μg litre^{-1} and their total content exceeded 3 mg litre^{-1} which was approximately 10–100 times greater than their content in water samples from the same region. An analogous result was observed for aromatic hydrocarbons. On the other hand phenols, widely represented in water, were practically absent from snow samples with the exception of phenol itself and dimethylphenols. Data on the content of certain organic compounds present at the highest concentrations in snow and water samples are given in Table 2.

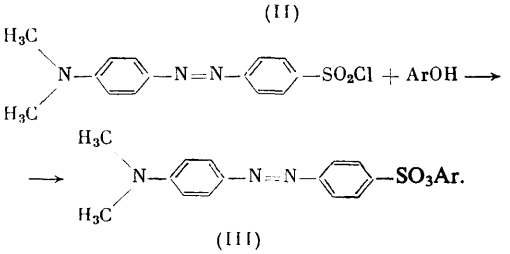
It is possible to explain the similar character of the distribution of contamination in the given region by the theory of the adsorption of organic compounds by dust particles suspended in the atmosphere.[10] The process for the transfer of organochlorine pesticides, polychlorinated biphenyls and polynucler aromatic hydrocarbons, which occurs in this way, has been studied previously.[10] Carbon dust, present in the atmosphere of Kemerovo, adsorbs organic compounds to a significant extent, having higher values of adsorption coefficients than activated carbon k_c. The value of $\lg k_c$ for higher alkanes and aromatic hydrocarbons is appreciably greater than for phenols, alcohols and ethers.[1]

Phenols, like hydrocarbons, belong to the group of widely distributed and highly toxic contaminants of natural waters. Chlorophenols are formed on chlorination of water, and their toxicity and ability to accumulate in organisms grows with increasing content of chlorine atoms in the aromatic ring.[1,11] Many phenols are detected in water by taste and smell at concentrations less than 0.1 μg litre^{-1}.[1]

From our data the detection limit for phenols when using CGC with a flame-ionisation detector was from 0.4–1.8 μg litre^{-1}, and by HPLC was several μg litre^{-1}, which frequently does not meet modern nature conservation requirements. It is possible to increase the sensitivity and selectivity of determining phenols by chromatographic methods if phenols are converted into various derivatives.[12] Thus the combined use of acetylation and pentafluorobenzoylation of chlorophenols and the use of an electron capture detector enables the quantitative determination of phenol in water at concentrations of 0.2–0.4 μg litre^{-1}.[13] With the aim of improving and clarifying the actual possibilities of the highly sensitive quantitative analysis of phenols in natural waters at the background level by CGC and HPLC, we have carried out a qualitative and quantitative determination of phenols as pentafluorobenzyl ethers (I), pentafluorobenzoyl (II) and dabsyl (III) esters.

$$C_6F_5CH_2Br + ArOH \longrightarrow C_6F_5CH_2OAr, \quad (I)$$

$$C_6F_5COCl + ArOH \longrightarrow C_6F_5COOAr, \quad (II)$$



(III)

Various esters and ethers of types (I)–(III) were synthesised and obtained in the pure state for the first time for this purpose. Their structures were demonstrated by elemental analysis, IR and NMR spectroscopy and mass spectroscopy.

It was established that the limits of detection of derivatives of types (I) and (II) by CGC using an electron capture detector were 1–2 mg and of derivatives (III) by HPLC 1–2 ng. For the quantitative determination of phenols as derivatives (I)–(III) we determined values of the relative factors for the detector signal in relation to the phenol derivatives and also established the so-called degree of detectability of phenols (i.e. the degree of conversion of phenols by the method). Limits of detection of phenols in natural waters were 10–100 ng litre^{-1}.

For the qualitative determination of phenols as derivatives (I)–(III) we studied their mass spectral decomposition by electron impact and for derivatives (I) by chemical ionisation with isobutane recording both the positive and negative ions. It was established that mass spectrometry enabled identification of phenols in nautral waters with a high degree of reliability.

The method of determining phenols as ethers of type (I) was tested by us when investigating water from the Moscow River in the spring of 1987 for the presence of phenols (Table 3).

Table 3. Content of phenols in water samples from the Moscow River.

Compound	LPC, μg litre^{-1}	Concentration in water, μg litre^{-1}
Phenol	1	2.9
4-Chlorophenol	1	7.7
4-Nitrophenol	20	1.4
Pentachlorophenol	10	103.9
2,4-Dinitrophenol	30	10.7

Identification of derivatives of phenols was carried out by comparing retention times of standards (pentafluorobenzyl ethers of phenols) at various temperature modes of chromatography and was confirmed by gas chromatography-mass spectrometry. As follows from the data of Table 3 the content of chlorophenols in the Moscow River exceeded the values of the limiting permissible concentrations (LPC) by 3–10 times. The contents of nitrophenols were somewhat lower than the LPC values.

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Problems of the development of ecological instrument making

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The attention devoted to the development of new analytical methods and instruments for ecology has been aroused by the appearance in the waste from economic activity of a large amount of highly toxic pollutants, which are dangerous to man and the environment even in very small amounts. The detection of these substances at the level of limiting permissible concentrations against the background of interfering substances is a very complex scientific and technical task. Bearing in mind that about 70 000 organic compounds are being used throughout the world and are therefore present in the environment and that their number increases by 1–2000 annually,[1] the necessity for newer modern approaches to ecological analyses becomes evident. For such studies, it is essential to have at one's disposal a set of fairly universal methods and instruments with a high sensitivity and selectivity. The results should be interpreted on a computer. Furthermore, it is essential to possess a data bank for the identification of substances.

The development of analytical methods in ecology has been stimulated by a series of accidents in chemical undertakings and by the results of their investigation. The results of a study of the accident in Seveso (Italy) in 1976,[2,3] where the latest advances in chromatography and mass spectrometry had to be used in order to detect traces of dioxins, which poison human beings and pollute the locality, have appeared in print to the greatest extent. The consequences of the agricultural pollution and of the use of chemicals (herbicides) during most recent wars have also served as stimuli.[4] All these major catastrophic pollutions have led to a sharp increase in the number of scientific publications on the development of analytical methods using the latest instruments: highly effective gas and liquid chromatograph and mass spectrometers, which are used in more than half the instances where analytical methods are needed.[5]

The increasing complexity of the ecological situation and frequent accidents in chemical undertakings have induced a rapid growth of the industrial manufacture of analytical apparatus in various countries. The quality of the apparatus has been increasing significantly as a result of a large number of service devices: devices for sampling and preparation of samples and a sophisticated system for the interpretation of data on computers with extensive program libraries, data bands, and systems for the identification of substances.

The achievements in instrument making and electronics enabled a number of firms to develop mobile laboratories equipped with chromatographs and mass spectrometers. The best known of these is the TAGA-3000 Laboratory (Canada). It uses as the detector a mass spectrometer with a device for the automatic injection of samples from the atmosphere, which ensures a high sensitivity (10^{-15} g cm^{-3}). The presence of a navigating device makes it possible to plot maps of contamination in the given locality. The MM-1 mobile laboratory of the Bruker Company (Federal Republic of Germany) has effective analytical characteristics. It uses as the detector a quadrupole mass spectrometer with sample injection through a capillary column and with heating at the sampling site. This laboratory is designed for the rapid identification and estimation of the amount of organic substances in water, air, and on the surface. It can be used to analyse the distribution of dioxins.[6]

The use of modern analytical methods and apparatus combined with well thought out organisational measures is undoubtedly the most promising trend in ecology, which has already frequently led to positive results, and not only in the case of industrial accidents already mentioned. The significant improvement of the ecological situation in the region of the Greak Lakes (USA) and the Mississippi River may serve as an example. The combination of modern physicochemical and biological analytical methods and international cooperation has made it possible to investigate fairly rapidly the causes of the death of seals in Lake Baikal.[7]

The use in ecology of the majority of analytical instruments is limited by their high cost, the need for special accommodation, and the unduly laboratory-oriented design of the instruments as well as the need for highly qualified specialists to carry out the analyses. For the mass application of analytical instruments in ecology, the designers must significantly reduce the cost of the apparatus without loss of their quality, reduce their weight and size, and expand their operating conditions.

The small batches of chromatographs and mass spectrometers produced by Soviet industry do not satisfy the requirements of ecologists either as regards their functional possibilities or their operating characteristics. Essential instruments such as chromatograph-linked mass spectrometers and quadrupole mass spectrometers are not produced at all. There is a particularly serious lack in the field of assembly and interpretation of data on the basis of modern advances in computer techniques. Devices for continuous monitoring based on laser techniques and small cheap and selective sensors of different types are completely lacking.

One of the main reasons why Soviet industry lags behind in ecological instrument making is the absence of a scientific-technical base and of permanent specific organisational stimuli, which, on the one hand, would stimulate the demand for ecological instruments because of the need to carry out measures to protect nature and, on the other hand, would stimulate the manufacture and improvement of their quality.

The Siberian Division of the USSR Academy of Sciences prepared the program "Development of Methods, Instruments, and Mobile Laboratories for the Analysis of the Pollution of the Environment", which can be regarded as the first stage of work designed to create a