ANALYSIS OF EXTRACTABLE ORGANIC POLLUTANTS IN THE UPPER VOLGA WATER

Yu.P. Turov, I.D. Pirogova, and P.B. Kadychagov

Institute of Oil Chemistry,
Siberian Branch of the Russian Academy of Sciences, Tomsk

Received January 25,1994

Chloroform–extractable organic pollutants in the Upper Volga water were studied by the use of gas chromatography/mass spectrometry and optical spectroscopy techniques. Analysis of organic extracts was carried out by Method 625 EPA USA. Downstream variations pattern of the abundance of some organic compound classes is shown.

In attempting to trace the prospects and avenues of development of analytical methods for environmental monitoring, one cannot but infer that instrumental and remote monitoring techniques, which feature fast data processing times comparable in duration with the process of measurement itself, have undeniable advantages over other methods. These methods are, as a rule, indirect ones; they largely rely on observation of certain physical characteristics of the environment that are bound with functional dependence to the occurrence and abundance of the compound detected.

The performance behavior of novel instrumental methods is generally tested using sets of standard samples of known composition and concentrations of compounds analyzed. However, on attempted use of instruments with superior laboratory performance behavior in actual practice (by *in situ* testing), a significant discordance is occasionally observed between the results obtained and analytical quality assurance/quality control (Qa/Qc) procedure data.

In the majority of cases, a discrepancy of this kind can be attributed, for the most part, to the presence in the sample analyzed of components other than the ones included into the set of standard samples as target compounds. Moreover, in view of the existing trend towards increasing range of potential environmental pollutants, it is highly probable that Qa/Qc techniques also provide incorrect results for the same reason. It seems unlikely yet, even in theory, that availability of standard samples representative of the vast range of potential environmental pollutants might be possible.

Therefore, in order to find out the probable sources and causes of disagreement between data provided by different methods and to make a qualified decision about the given method's ability to meet a particular analytical challenge pertaining to environmental monitoring, it is necessary, or at least desirable, to perform screening survey testing of the region (proving ground) under study using the most comprehensive procedures that are not optimized for a particular compound or class of compounds. The fact that these methods are not *a priori* directed to detecting a limited range of target compounds allows one to obtain an overall picture of environmental pollution and to define probable interference and error sources.

Analysis of organic matrices in natural water is one of the most significant analytical challenges. First and foremost, the task of analyzing for a wide spectrum of pollutants is complex in itself. Thus, today a vast number of chemicals and their degradation and metabolism products are found to occur in the environment. Over 100 000 various chemical pollutants could be detected in the air and water, providing adequate means, manpower and facilities requisite for investigation of this kind are available.[1] Furthermore, the analytic task is complicated by the fact that organic pollutants mostly occur in water in dissolved or solvated state, which often necessitates use of multistage sample preparation procedures, i.e., isolation and concentration of organic pollutants prior to carrying out analysis proper.

Isolation and concentration of organic impurity occurring in water is accomplished by such methods in common use as extraction and absorption techniques employing various adsorbents. The absorption technique offers a relative case of sample preparation, which is especially advantageous under field testing conditions; however, this method's utility is limited by a certain degree of selectivity exhibited for various organic compound classes. Therefore, liquid––liquid extraction was the technique of choice used to carry out the first preparative step in that study. This permitted semi–quantitative assessment to be made of the total pollution of water with various organic compound classes.

Since oil products are the major organic pollutants of environmental concern in surface water of most regions that are strongly affected by human activities, their quantitative analysis in the water samples studied was performed using an Environmental Control Agency procedure.

Extractable organic pollutans in the Upper Volga water were examined by researchers of Institute of Oil Chemistry, Siberian Branch of the Russian Academy of Sciences, Tomsk. Sampling and sample preparation were accomplished in the course of a Moscow–Nizhny Novgorod–Tver–Moscow trip onboard the ship "Il'ya Repin" over the period from June 28 to July 8, 1993. Analyses were performed in the Institute's laboratories.

Following a common world–wide practice, we selected gas chromatography/mass spectrometry (GC/MS) as the technique of choice for surveying environmental organic pollutants in the Upper Volga water. Owing to its excellent performance characteristics, i.e., low detection limits, high sensitivity, linear dependence of signal intensities *vs.* compounds concentrations preserved over a wide dynamic range), the GC/MS method is a unique tool for analysis and identification of virtually the whole spectrum of organic pollutants capable of passing through a chromatographic column under the actual chromatographic run conditions.

0235-6880/94/04 271-04 $02.00

Studies on the matrices of organic pollutants, whose occurrence in natural water is largely due to the anthropogenic factor, were carried out according to the following analysis scheme: sampling, extraction of organic pollutants from aqueous medium, clean–up of the extract, concentration, qualitative identification, and semi–quantitative determination of individual compounds by gas––liquid chromatography and GC/MS methods.

Use of such highly informative methods allows one to determine for a given sample a wide array of organic pollutants varying with respect to their structural and functional–group composition and molecular masses.

1. INSTRUMENTATION AND METHOD DESCRIPTION

Analysis of surface water samples for the extractable organic pollutants was accomplished by a procedure, which essentially follows USA Environmental Protection Agency (EPA) Method 625 (see Ref. 2); the analysis scheme is shown in Fig. 1.

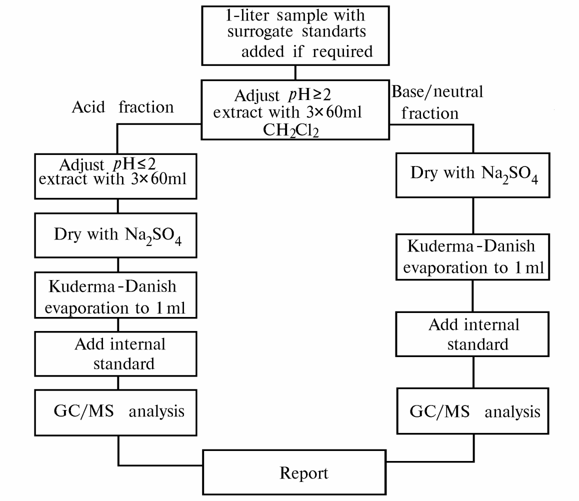

FIG. 1. Diagram of the main steps of the analytical procedure used to determine organic pollutants content in the Upper Volga water samples.

A two–litre water sample to be analyzed was placed into a five litre glass vessel pretreated by standard techniques and pH adjustment was accomplished using 40% NaOH solution. When pH became equal to 12.0, an aliquot of chloroform was added and the vessel was vigorously shaken for 5 min and then the solution was allowed to settle for 5 min. Sample separation was performed in a separating funnel and the resulting extract was collected into a separate vessel. Following two additional consecutive extractions using chloroform, concentrated hydrochloric acid was added to the sample analyzed till pH of the medium became equal to 2.0 and then extraction from the acid medium was carried out again using the above procedure. The "acid" and "alkaline" extracts were collected into separate vessels. Their drying was accomplished by passing them through a sodium sulfate column and their volume was brought up to 0.2 ml by evaporation with a rotor evaporator.

GC/MS analysis efficiency is known to depend in many ways on water sample preparation; therefore, particular care was taken in performing these steps.

Selection of chloroform as the extraction solvent of choice is attributable to its obvious advantages of availability and suitability as the solvent for virtually all organic compound classes. Another significant parameter that affects the method's performance behavior is solvent purity grade as the result of the chloroform multiple distillation followed by solvent quality control by GC/MS.

To preclude any chance of extraneous impurity getting into the sample analyzed, the chemical glassware was pretreated by washing with surfactants followed by careful rinsing with water and by soaking in freshly prepared solution of potassium bichromate in concentrated sulfuric acid and finally by washing with several portions of distilled water and by steaming in the vapors of water subjected to two successive distillations.

Anhydrous sodium sulfate employed for drying the extracts was calcined before use in a muffle furnace at 105°C for 6 hrs. Analyses were performed on an R–10–10C model NERMAG quadrupole GC/MS instrument (France) that features a capillary column directly coupled to a mass analyzer without resort to a separator.

Instrument operation

Chromatograph: a Chrompak capillary chromatographic column 26 m×0.22 mm i.d. coated with CPSil–5 phase (film thickness of 0.13 μm); helium carrier gas; inlet pressure 0.5 atm.; evaporator temperature 220°C; interface temperature 230°C; programmed heating of chromatograph thermostat: T_{init} of 80°C is maintained for 2min., then heating is carried out at a rate of 4°/min to $T_{\max}$ of 280°C and the isothermic conditions are maintained until the column is completely free.

Mass spectrometer: electron impact ionization; electron energy 70 eV; temperature of ionization chamber 230°C; range of masses registered from 33 to 500 a.m.u.; mass spectrum scanning duration 0.4 s.

Identification of pollutant components was performed from their mass spectra using spectral–structural correlations established by empirical methods, which were taken from a literature search, as well as USA EPA/NIH computer library storing about 34 000 mass spectra.

Quantitative analysis was accomplished by the use of deuteroacenaphthen and chrysene as internal standards, the respective chromatographic peak areas being taken into account.

Identification of pollutants was carried out using the board spectrum approach. In the case several isomers having similar mass spectra were present, their chromatographic characteristics, i.e., retention times, retention indices according to Kovač, etc., reported in literature or obtained in model runs were used for identification.

Analysis for oil products in water samples was accomplished in the Institute's laboratories in accordance with Refs. 3 and 4 using a "Specord M 80" infrared spectrophotometer.

Spectra of compounds eluating from an alumina column were recorded at 3500–2500 cm^{-1}. The lower detectable limit was 0.01 mg/l.

2. RESULTS AND DISCUSSION

Table I shows the results of analysis for oil products in surface water samples with times and sites of sampling indicated. Sampling was performed using shipborne instrumentation of "Taifun" group.[5]

Table II gives the results of analysis for organic compounds in surface water samples that were obtained by chromatographic and GC/MS techniques.

TABLE I. Sites and times of sampling and oil products contents in the Upper Volga water samples.

No.	Sampling site	Date and time of sampling	Oil products content, mg/l
1	Kostroma, traverse of warf No. 3	June 30, 1993 19.10	0.68
2	N. Novgorod, Oka river, roadstead on Kremlin	July 1, 1993 13.00	1.56
3	N. Novgorod, Volga river, 500 m upstream of Strelka	July 2, 1993 19.15	0.96
4	Ples, Volga river	July 3, 1993 19.30	1.05
5	Yaroslavl, Volga river, on sailing from warf	July 4, 1993 18.45	0.60
6	Rybinsk reservoir, upstream of lock	July 4, 1993 24.00	0.91
7	Tver, in sailing from warf	July 6, 1993 18.45	3.10

TABLE II. List and contents of compounds (μg/l) *identified in chloroform organic extracts from the Upper Volga water samples.*

No.	Compound	Sampling site					
		Tver	Rybinsk reservoir	Ples	Yaroslavl	N.Novgorod, the Oka	N.Novgorod, the Volga
1	2	3	4	5	6	7	8
	Phthalic ethers:						
1	Diethyl phthalate	2.1	0.5	2.3	15.0	3.5	53.1
2	Dibutyl phthalate	10.5	36.5	126.6	210.0	48.5	449.3
3	Diisooctyl phthalate	3.8	8.2	20.1	62.5	6.8	55.4
4	Other dialkyl phthalates	6.3	0.6	6.6	54.2	5.0	12.0
	Paraffins:						
5	Dodecane	0.1	0.5	0.5	1.5	1.0	0.1
6	Tridecane	0.3	1.9	1.9	3.2	2.0	0.6
7	Tetradecane	2.1	4.6	4.1	5.9	5.8	3.5
8	Pentadecane	3.3	6.7	7.8	10.3	6.4	7.9
9	Hexadecane	5.8	8.0	12.3	18.1	6.7	13.7
10	Heptadecane	3.6	6.4	9.7	15.6	4.3	13.9
11	Octadecane	3.1	4.2	7.4	13.1	3.2	10.3
12	Nonadecane	3.0	3.5	4.4	12.8	2.1	9.3
13	Eucosane	4.3	4.1	5.0	13.0	3.8	12.9
14	Geneucosane	4.8	4.3	6.4	13.0	3.0	11.4
15	Docosane	4.7	4.5	6.5	11.5	3.2	9.3
16	Tricosane	5.5	5.0	9.3	15.3	4.1	10.5
17	Tetracosane	5.0	4.8	9.0	12.6	3.3	8.3
18	Pentacosane	4.1	4.0	7.7	10.1	2.1	6.0
19	Hexacosane	3.2	3.0	6.5	10.0	1.6	5.1
20	Heptacosane	2.0	1.5	4.4	7.3	1.0	3.5
21	Octacosane	1.0	0.6	3.0	6.5	1.0	2.0
22	Nonacosane	–	–	1.8	6.0	0.9	1.7
23	Tricontadecane	–	–	1.0	5.5	0.2	1.5
24	Isoparaffins	9.5	15.6	24.5	28.6	19.6	60.0
25	Alkyl naphthenes	8.6	6.0	13.4	10.9	10.1	15.0
	Aromatic hydrocarbons:						
26	Naphthalene	0.3	0.2	–	0.5	0.4	0.1
27	Methylnaphthalenes	0.1	0.1	–	0.3	0.2	0.15
28	C_2–alkyl naphthalenes	0.1	0.1	0.1	0.1	0.1	0.1
29	C_3–alkyl naphthalenes	0.06	–	–	0.1	–	–
30	Tetralin	0.8	0.05		1.2	0.1	0.07
31	Acenaphthene	0.2	–	–	1.1	–	0.21
32	Dihydroacenaphthene			0.1	0.2		
33	Diphenyl	0.3	0.2	–	0.8	1.0	0.8
34	Diphenyldiethyl	0.05			0.1		
35	Fluorene	0.1	0.1	0.1	0.3	0.6	0.5
36	Anthracene (phenanthrene)	0.1	0.1	–	0.2	0.1	0.3
	Phenols:						
37	Cresols	0.9	0.2	0.5	3.5	4.2	3.0
38	Alkyl phenol (m = 220)	1.1	0.1	0.6	3.3	1.8	1.1
39	Alkyl phenol (m = 234)	1.4	0.1	4.2	2.8	1.9	8.5

Table II (continued).

1	2	3	4	5	6	7	8
40	Chlorophenol	0.1	–	–	1.2	0.5	1.6
	Carboxylic acids:						
41	Caproic acid	60.2	2.1	10.2	8.4	4.2	5.3
42	Lauric acid	44.5	10.6	16.5	45.0	9.4	12.6
43	Myristic acid	82.0	15.2	18.3	51.0	16.0	24.5
44	Palmitic acid	410.0	73.5	160.0	143.0	60.0	126.0
45	Stearic acid	91.6	18.1	56.0	112.0	23.1	80.0
46	Oleic acid	112.0	10.3	94.0	96.0	10.1	145.0
	Ethyl ethers of fatty acids:						
47	Ethyl laurate	0.8	1.0	6.8	2.5	1.8	1.3
48	Ethyl myristate	3.0	–	4.5	6.8	1.3	4.6
49	Ethyl palmitate	15.6	3.8	12.3	15.5	8.5	10.2
50	Ethyl stearate	4.5	–	5.2	5.3	1.1	2.0
	Ethers of other organic acids:						
51	Methyl ether of cyclohexene (dimethyl–oxohexyl) carboxylic acid	4.6	0.8	2.2	5.2	6.8	0.3
52	Ethyl oleate	8.1	3.6	16.5	11.6	7.4	71.0
	Other organic compounds:						
53	Dibenzofuran	3.3	–	–	4.5	6.2	5.4
54	Triphenyl phosphate	7.5	3.2	5.0	5.6	2.6	6.8
55	Methyl triphenyl phosphate	2.3	1.1	2.8	4.5	1.1	4.6
56	Dimethyl triphenyl phosphate	1.0	0.6	1.1	2.1	0.6	2.1
57	Trimethyl triphenyl phosphate	0.2	–	–	0.5	–	–
58	Nitrotoluenes	0.2	0.1	–	0.9	0.8	0.5
59	Aldehydes	18.9	2.3	5.7	21.8	23.5	10.5
60	Higher alcohols	12.1	3.4	1.8	26.5	15.0	6.5

In accordance with a common practice adopted in Russia, water quality and pollutants level are assessed by comparing the results obtained by comparison with maximum permissible concentration (MPC) of pollutants in water that are promulgated by the Federal Sanitation and Environmental Agency. In modern world–wide practice, priority pollutants level is intended for application in environmental analysis alongside maximum permissible concentrations specified by law within rigid limits.

A priority pollutants list comprises chemical compounds with regard to their toxicity, frequency of occurrence in a given region, production output, utilization, stability to dissipation and degradation processes to give nondeleterious products as well as their capability of being analytically determined in natural environment.[2] Therefore, in assessing the total pollutants level in surface water in general, and in the Upper Volga water in particular, it is thought expedient to incorporate into the list of pollutants to be analyzed not only highly toxic substances but also the ones for which no maximum permissible levels have been promulgated as yet.

The results of analyses for oil products in water samples obtained by our researchers show good agreement with those of "Taifun" group.[5] Deviations observed in some cases might have resulted from particular features of sample preparation procedure as well as from natural variations in oil products contents found in the surface water over the river's expanse at a high total pollutants level.

The total pollutants level in the Upper Volga water might be evaluated as medium to high, no significant downstream variations being observed in the organic matrices. Due to intense arterial navigation, oil products levels found in the water over the whole river area are much higher than MPC of pollutants in water (0.3 mg/l). Variations in the abundance of other organic pollutants are probably due to the pattern of location of their sources of input to the river–basin as well as to the downstream transport of pollutants.

REFERENCES

1. S.R. Heller, in: *Practical Mass Spectrometry* (Plenum Press, New York, 1979), pp. 219–240.
2. W.W. Shackelford and J.M. Mc Guire, Spectra **10**, No. 4, 17–21 (1986).
3. List for Approved Methods for Determining Pollutants Levels in Natural and Sewage Waters, No. 13–3–05/75 (1988).
4. *Environmental Protection. Hydrosphere. Determination of Oil Products Contents in Natural and Sewage Waters by IR Spectrophotometry.* OST 38.01378–85. Moscow.
5. S.P. Belyaev, L.A. Lastochkina, G.M. Khomushku, et al., Atmos. Oceanic Opt. **7**, No. 4, 497–511 (1994).