

PREREVIEW OF MANDATORY METHODS FOR DETERMINATION OF SELECTED ORGANIC COMPOUNDS

Alica BARTOŠOVÁ - Maroš SIROTIK - Lenka BLINOVÁ

ABSTRACT

Hydrosphere contamination of the environment by organic substances is increasing. It increases not only the concentration but also the amount and harmfulness. Persistent organic pollutants are substances that have the ability to remain in the environment. They are capable of long-term transport, bio-accumulation in plant and animal tissues. To the substances belong compounds such as dioxins, furans, PCBs and organochlorine pesticides. POPs released into the environment can be transported by air or water to areas that are often very far from the place of their origin. In these areas, POPs concentrate in living organisms, including humans, at concentrations that can harm human health. The aim of the paper was to process the research for the presence of organic matter in the water and on the methods of determination, in particular the use of gas chromatography with mass detector and infrared spectroscopy with Fourier transform.

KEY WORDS:

method, extractive substance, polycyclic aromatic hydrocarbons, phenols, polyphenols, halogen derivative

Introduction

In waters, organic matter may be natural or anthropogenic origin:

- naturally occurring organic matter may be included extracts from soils and sediments (mainly humic substances – peat humus and soil, extracts from the leaves and smoldering wood) and products of different organisms. The microorganisms and algae in their life activity produce a number of substances, in particular sugar-based, protein, amino acids, polyphenols, hydroxamic acids and the like. Some substances have surfactant properties and some that arise especially life activity of cyanobacteria are toxic and odour causing,
- anthropogenic organic compounds originate from sewage and industrial wastewater, wastes from agriculture, landfill and can also occur in water treatment by chlorination.

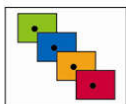
From the hygienic point of view it is necessary to distinguish substances subject to (i) biodegrade in water and in sewage treatment; and (ii) biochemically resistant materials, such as polyhalogenated organic compounds, lignin polycyclic aromatic hydrocarbons, certain pesticides and surfactants, complexing agents and others. Water pollution biologically recalcitrant substances is undesirable, as they can pass through to the drinking water. Organic substances may significantly affect the chemical and biological properties of water [1].

This includes:

- substances with carcinogenic, mutagenic, teratogenic or allergenic effects (e.g. some polyaromatic hydrocarbons and pesticides, polychlorinated biphenyls),
- substances affect the colouring of water (humic substances, dyes, lignin),
- substances affect the smell and taste of water (hydrocarbons, chlorinated hydrocarbons, chlorophenols, substances produced by some microorganisms in the proliferation of such algae and actinomycetes),
- substances affect foaming water (surfactants, lignin),
- substances create a surface film on the surface and thereby impair the transfer of oxygen into the water (petrol, oil),
- substances affect the complexing capacity of the water and thus desorbed toxic substances from sediments [1].

The organic water pollution is evaluated according to the summary of determination (COD_{Mn} , COD_{Cr} , DOC, non-polar extractable compounds, anionic surfactants, humic substances) and by determining the number of selected toxic chemical species (some aromatic hydrocarbons – benzene, toluene, xylene, ethylbenzene, styrene, etc. [1]. A particular group of these pollutants are **persistent organic pollutants** which are found in aquatic ecosystems. Persistent organic pollutants are substances remaining in the environment, they are capable of long-term transport, bioaccumulation in plant and animal tissues. Among the substances belonging to this group can include compounds such as dioxins, furans, PCBs and organochlorine pesticides[2].

The main sources of POPs are industry, households, transport, and waste disposal, such as incineration or landfill [3]. In monitoring the effects of POPs on human body was found an association between exposure to POPs and cancers, skin diseases, nervous and mental disorders, changes in the immune system, reproductive disorders etc. Very adversely affect the substances in human tissues. They can accumulate in breast milk, and then penetrate into the body of the infant. Even at the minimum concentration (on the order ppt) adversely affect brain development.



IPCS (1995) divided the 12 major POPs into three groups:

- pesticides – aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex, hexachlorobenzene and toxaphene),
- industrial chemicals – PCBs and hexachlorobenzene,
- undesirable by products – dioxins and furans [2].

1. Extractive substances (ES)

Significant organic pollutants that adversely affect water quality are extractable substances (ES), which are low soluble in water and good soluble in organic solvents. ES are divided into two groups: the compounds (i) **polar** and (ii) **non-polar**, depending on the molecule carries an electric charge, dipole or as a whole electroneutral, or the dipole moments of the bonds in the molecule are deleted. For analytical determination all extractable components are separated in polar sorbent adsorption (e.g. silica gel) which adsorbs only PEL (polar – hydrophilic extractable substances) and NEL (non-polar – lipophilic extractives) remain in the organic solvent solution [4].

To determine the ES is used spectrophotometric method in the infrared spectrum after extraction to Ledon described by the standard STN 83 05404 – Chemical and physical analysis of waste waters. Determination of crude oil and oil products. Determination of crude oil and oil products or gravimetry according to STN 83 05405 – Chemical and physical analysis of waste waters. Determination of extractable matters. Determination of extractable organically bound chlorine is done according to STN 75 7530: 1991 – Water quality. Determination of extractable organic halogens (EOX) [5, 6].

1.1. Non-polar extractive substances (NES)

NES are the main source of products derived from the crude oil: gasoline, kerosene, diesel fuel, combustion and lubricating oils, fuel oil, and asphalt, which are composed primarily of hydrocarbons as n-alkanes, iso-alkanes, cycloaliphatic and aromatic hydrocarbons. The petroleum hydrocarbons usually lacking alkenes and alkynes. Hydrocarbon mixtures are: from C₄ to C₁₂ for gasoline, from about C₁₂ to C₁₈ for kerosene from about C₁₈ to C₂₄ from combustion of oil and from C₂₄ to C₄₀ for lubricating oils. In the bottom sediments of lakes and rivers they were also found alkanes and alkenes biogenic origin, resulting from the extensive production of phytoplankton – that small amounts are natural components of water and therefore abandoning the concept of “the determination of oil” [7].

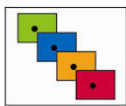
Producer of other significant non-polar extractable substances, non-petroleum origin is the wood processing industry [1]. The most significant negative effects of these substances is affecting the taste and odour in the water, and is already in a concentration of 0.05 mg L⁻¹. They also affect the taste of fish meat because they have the ability to accumulate in some aquatic organisms and bottom sediments. In higher concentrations to form the emulsion, a film or a continuous layer, (the formation of the film occurs on the surface of oil at a concentration of 0.1 to 0.2 mg L⁻¹). The oil film on the surface of deteriorating transmission of oxygen from the atmosphere into the water, thereby negatively affecting the self-cleaning. NES solubility in water depends on several factors, e.g. type of hydrocarbon, temperature, pH, salt content, etc. With increasing temperature the solubility is increased and with increasing salt content in the water is decreased [8]. Toxic effects of these substances on aquatic organisms is different, for example normal petrol affects the trout toxicity at concentrations of 100 to 260 mg L⁻¹, gasoline already at 40– 100 mg L⁻¹, kerosene is toxic to fish at concentrations of 10 mg L⁻¹, diesel oil at 50 to 100 mg L⁻¹ and toluene at 10 mg L⁻¹.

NES determination is non-specific screening method, which includes hydrocarbons, as well as other non-polar substances (organic halogenated derivatives and nitro derivatives). Difficult assessment of the results is one of the main drawbacks of this group determination. Therefore, the determination of NES is not normally part of the chemical analysis of water, it is relevance indicator. In different areas and for different purposes has been used [1,7]:

- *gravimetric method*
- *spectral*– spectrometry in ultraviolet (UV) spectrum, electromagnetic radiation spectrometry and infrared (IR) spectrum of electromagnetic radiation,
- *chromatography*– gas chromatography combined with mass spectrometry (GC-MS) and high performance liquid chromatography (HPLC),
- *biochemical*– particularly immunoassay-analysis.

The indication of the different toxicological relevant substances in a total amount of NES is required to use chromatographic methods. When using IR-ending, it is necessary to take into account that the health harmful aromatic hydrocarbons absorb in the IR spectrum – region less spectrum [1]. In the past, as the most suitable solvents was used carbon tetrachloride (CCl₄) [7] and S 316 (1,2,4,4-tetrachloro-1,1,2,3,3,4- hexafluorobutane) [9].

EPA recommended for the determination of NES A Method 1664 N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM / non-polar Material) by Extraction and Gravimetry– Revision A, which is also used for determining polar extractable compounds. This method can be used for analyse of polar extractive substances. According to EN ISO 15680: 2005 (75 7513) number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using the “purge and trap” and thermal desorption can be determinate by this method, and



1.2. Polar extractive substances (PES)

Most often these are of natural origin, especially fat, some pharmaceuticals, surfactants and detergents [20,21]. The high concentrations are found mainly in water and sewage in some industrial wastewater.

Lipids, fats and oils are esters of fatty acids and alcohols, the molecules are relatively poor in oxygen. They form a very diverse group of substances whose common feature is their solubility in organic solvents, but only partial solubility, respectively, complete insolubility in water. They have a relatively low melting point. They are essential for the construction of cellular structures and tissues, a source of energy for the body, protecting the body from heat loss and mechanical damage, participating in the construction of nerve cells and coat the nerve fibres, creating an environment in which the soluble substances or water insoluble (certain vitamins, hormones, drugs, colouring agents).

The alcohol component is an alcohol glycerides – glycerol propanetriol. It is a trihydric alcohol, therefore, may be esterified with the three OH groups of [10]. Typical polar extractable substances includes pharmaceuticals.

According to STN 75 7566: 2007 gravimetric method to determine the total fats and oils in water can be used. This assay method is an adaptation of EPA Method 1664, *Revision A: N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Trated N-Hexane Extractable Material (SGTHEM; Non-polar Material by Extraction and Gravimetry)*.

2. Polycyclic aromatic hydrocarbons (PAH)

PAHs are a group of organic compounds having two or more condensed benzene rings in the linear, angular, or a cluster arrangement, which may be additionally substituted [8].

PAHs are usually classified by origin, on (i) *petrogenic* (most often resulting degradation of complex organic compounds) and (ii) *pyrogenic* (associated with combustion processes). Petrogenic example naphthalene, fluorene, phenanthrene, chrysene, and dibenzothiophene are derived from hydrocarbons and enter the environment, in particular in their processing. They are produced commercially as chemicals. Pyrogenic PAHs such as anthracene and benzo(a)pyrene formed as a by-product of incomplete combustion of organic materials such as various fossil fuels, wood, but also arise in forest fires or volcanic activity.

High contamination of the surrounding area are characterized by a coking plant, where in the absence of oxygen burns coal to produce coke. Hydrocarbons from combustion processes is mainly contaminated atmosphere, where the dry and wet deposition to water and soil. Water and soil are contaminated directly from industrial effluents, especially when emergencies arise due to technical failures and operator errors during transport, handling and storage of oil and oil products. There is also a third category – PAU of biological resources that arise in diagenesis of organic matter [11]. PAU impair the organoleptic properties of water and can be toxic. Adsorption ability of hydrocarbons can significantly affect their migration in the environment, so they accumulate in sediments. Is the most damaging of these six PAHs –fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene[8].

It is often complicated to define the sources of PAH contamination in waterways and coastal areas that have limited water circulation, particularly where multiple point sources co-occur with persistent non-point sources (i.e., urban areas or areas that have high ambient background levels). In such situations, the potential contributions of all possible point or non-point sources should be considered.

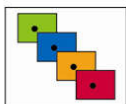
The use of methods of analysis requires three basic steps: (i) extraction and isolation of the PAHs from the matrix, (ii) cleaning the impurities from the PAHs and the fractionation and (iii) the identification and the determination of the components in each of the subgroups [12].

Determination of PAHs is most often done or the high – performance liquid chromatography (HPLC) with a fluorescence detector (FLD), or gas chromatography (GC) with a mass selective detector (MSD) after the extraction of the liquid or solid phase according to ISO 17993: 2004 (75 7512) [6, 13].

Supercritical fluid extraction (SFE) to the isolation of the analyte using the unique property of supercritical fluid liquid, which is formed under certain conditions of CO₂. This liquid is behaves like a gas and liquid in one and a non-polar character. Therefore it used in the extraction of non-polar compounds. After isolation of the analyte, it is necessary to do further analysis in order to determine the content of individual PAH in the sample, which is used for gas chromatography [6,13].

EPA recommends for determining PAHs these methods [14,15]:

- Method 550: *Determination of Polycyclic Aromatic Hydrocarbons in Drinking Water By Liquid-Liquid Extraction and HPLC with Coupled Ultraviolet and Fluorescence*
- *Detection,*
- Method 550.1: *Determination of Polycyclic Aromatic Hydrocarbons in Drinking Water by Liquid-Solid Extraction and HPLC with Coupled Ultraviolet and Fluorescence Detection,*
- Method 610: *Polynuclear Aromatic Hydrocarbons, Method 1654, Revision A: PAH Content of Oil by HPLC/UV,*



- Method 8272: *Parent and Alkyl Polycyclic Aromatics in Sediment Pore water by Solidphase microextraction and Gas chromatography/Mass spectrophotometry in Selection ion monitoring mode.*

3. Phenols and polyphenols

Phenols are organic compounds containing one or more hydroxyl groups bonded directly to the aromatic ring. These are chemically stable compound of an acidic nature, a relatively good solubility in water. They have a strong complexon properties, causing a yellow to brown colour [8]. Phenols have a high toxicity to aquatic organisms, already small concentrations can affect the taste of fish flesh [1].

High concentrations of phenols are found in some industrial waste water, for example thermal treatment of coal and petrochemical industry. They are part of some disinfectants and preservatives.

From the point of view of water management are very important reactions that occur in the chlorination of water, which can be formed intensively malodorous chlorophenol (from an organoleptic point of view can completely spoil drinking water [1]. One of the groups of toxic phenolic compounds are *nitrophenols*.

Spectrophotometric determination of phenol by reaction with 4-aminoantipyrine after distillation is carried out according to STN ISO 6439 (75 7528). The method allows the phenols themselves, but also fenolytic substances with a -ortho and -meta positions. Depending on the pH can be further fixed with a cast phenols -para position, where the substituents are halo-, carboxy-, methoxy-, and sulfo- group. The phenols have the para-position occupied by alkyl-, nitro-, benzo-, or aldehyde-, it is not possible to determine by this method. Selected monobasic phenols are set according to STN ISO 8165-1: 1996 (75 7529) Gas-chromatographic method after enrichment by extraction.

Furthermore, according to EN ISO 7523 down 75 selected alkylphenols using the extraction liquid – liquid and gas chromatography mass spectrometry [5, 6]. EPA provides for the determination of phenol:

- Method 8270C: *Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)*,
- Method 8041: *Phenols by Gas Chromatography*,
- Method 420.1: *Phenolics (Spectrophotometric, Manual 4-AAP With Distillation)*,
- Method 420.2: *Phenolics by Automated Colorimetry. Official Name: Phenolics, Total Recoverable (Colorimetric, Automated 4-AAP with Distillation)*,
- Method 420.4: *Total recoverable phenolics in water by semi-automated colorimetry. Official Name: Determination of Total Recoverable Phenolics by Semi-Automated Colorimetry*,
- Method 528: *Determination of Phenols in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS) – Revision 1.0*,
- Method 604: *Phenols*.

4. Halogenated organic compounds

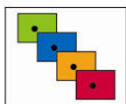
It is usually used for halogen labeling X. Distinction is made between these groups organically bound halogens:

- TOX – Total organic halogens,
- DOX – Dissolved organic halogen,
- AOX – Adsorbable organically bound halogens,
- EOX – Extractable Organically Bound Halogens,
- POX – volatile organically bound halogens,
- TX – total halogens [16].

Environmental pollution by halogenated organic compounds is in the forefront especially for water managers. This is the most toxic substances, some of which, in particular, aliphatic and aromatic polychlorinated derivatives may be potentially mutagenic and carcinogenic effects [17]. The toxicity of halogenated organic compounds (TOX), most of which belongs to the priority pollutants, and the frequency with water in order to lead to the determination of their summary in which would be needed immediately identify the components. In this summary, the determination of halogenated organic substances first isolated by adsorption or extraction.

The basic principle of organic halogenated empirical determination is the incineration in a stream of oxygen (or a mixture of oxygen and inert gas) at about 1000 °C, typically to the terminal microcoulometric argentometric titration of the released HCl, HBr, and HI. The results are usually expressed in equivalent concentration by weight of chloride [16].

Fluorinated organic compounds that procedure cannot be determined due to the solubility of the AgF. L. Koller. et al. [18] compares different methods for the determination of fluoride in drinking water and surface water by ion selective electrode (ISE), spectrophotometric determination or determination by ion chromatography. The results of spectrophotometric determination depends on the use and response without understanding the method for setting are unmatched. AOX is conventionally described. The indicator is useful for monitoring water quality. It is the amount of organic compounds containing bound chlorine, bromine and iodine, which under specific conditions are adsorbed on activated carbon [16]. The practice is most often used as chloride AOX microcoulometric after their adsorption on activated carbon and combustion in oxygen flow according to EN ISO 9562: 2005 (75 7531). According to EN ISO 10301: 1999 (75 7533) by GC methods can determine the volatile halogenated hydrocarbons and according to EN ISO 6468: 1999 (75 7501)



sets out selected organochlorinated insecticides, polychlorinated biphenyls and chlorobenzene GC method after liquid-liquid [6].

The POX assays, the sample of water in a flask at a temperature selected was purged with oxygen, which leads directly into the combustion tube of the analyser.

The determination of specific systems, the non-polar organic halogen derivatives, first isolated by extraction, and then the extract was charged in a combustion chamber. Disadvantage of this process is the relatively low yield of a wide range of organic halogenated. The values of specific systems are usually lower than the values of AOX, so that the setting is not used [16]. EPA recommends the determination of organic halogenated by:

- Method 501.1: *The Analysis Of Trihalomethanes In Drinking Water By The Purge And Trap Method*,
- Method 501.2: *Analysis Of Trihalomethanes In Drinking Water By Liquid/Liquid Extraction*,
- Method 8010B: *Halogenated Volatile Organics by Gas Chromatography - Revision 2*,
- Method 8011: *1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane by Microextraction and Gas Chromatography - Revision 0*,
- Method 1650: *Adsorbable Organic Halides by Adsorption and Coulometric Titration*,
- Method 9020B: *Total organic halides (TOX)*,
- Method 9021: *Purgeable organic halides (POX)*,
- Method 9022: *Total organic halides (TOX) by neutron activation analysis* [15].

RESULTS

The aim of this paper was made a review about methods of determination selected organic compounds in water, especially usage of gas chromatography and infrared spectrometry.

Gas chromatography could be used for determination non-polar extractive substances according to STN ISO 11423: 2005 (75 7514), polycyclic aromatic hydrocarbons according to ISO 17993: 2004 (75 7512) and EPA Method 8272, phenols and polyphenols according to EPA Method 8270C and EPA Method 8041. As well as some halogenated organic compound could be determined by GC/MSD EN ISO 10301: 1999 (75 7533) and to EN ISO 6468: 1999 (75 7501) is useful method for determination chlorinated insecticides.

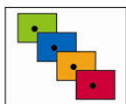
Infrared spectroscopy could be used for determination of extractive substances described by the standard STN 83 05404.

ACKNOWLEDGEMENTS

This contribution was written with the support of the Research and Development Operational Programme within the project: „Hybrid power source for technical and consulting laboratory use and promotion of renewable energy sources“ (ITMS 26220220056), financed from resources of the European Regional Development Fund.

REFERENCES

- [1] PITTER, Peter. *Hydrochemistry*, VŠCHT 1999, ISBN 80-03-00525-6, p.568.
- [2] Monitoring of POPs in the Slovak Republic, and technical report 2003.
- [3] HITES, R., *Persistent organic pollutants in the Great lakes*, Springer, 2006, p.422.
- [4] MALÝ, J.; MALÁ, J. *Wastewater Treatment*, ISBN 978-80-7399-785-4.
- [5] HOSTÍN, S. a kolektív, *Instrumental methods for environmental monitoring*, STU MtF, 2006.
- [6] GÜNZLER, H., GREMLICH, H. *IR Spectroscopy – An Introduction*, WILEY-VCH, 2002, ISBN 3-527-28896-1, p. 361.
- [7] LADOMERSKÝ, J., SAMEŠOVÁ, D., *Environmental impacts and analysis of oil products, the scientific studies*, 12, 2000/A, Zvolen p. 82.
- [8] ILAVSKÝ, J., BARLOKOVÁ, D., BISKUPIČ, F., *Water chemistry and Hydrobiology*, STU BA 2008, ISBN 978-80-227-2930-7, p. 304.
- [9] A. KOLLER, J., BINDZAR, J., BÍŽOVÁ, J., JANDA, V.: *Determination EL and NEL by gas chromatography and infrared spectrometry*. In: HYDROANALYTIKA 2005, p. 97.
- [10] HELDER, L., et al., *Theory and practice of food education in schools*, TU 2006, ISBN 80-8082-077-5.
- [11] THORSEN, W.A., COPE, W.G., SHEA, D., *Bioavailability of PAHs: Effect of soot carbon and PAH source*. Environmental Science and Technology, 2004.
- [12] Polycyclic aromatic hydrocarbons, U.S. Department of health and human services, Agency for Toxic Substances and Disease Registry, 1995.
- [13] *Determination of PAHs in the waters and sediments method SF-GC/MS*, Worksheets Department of Analytical Chemistry Palacký University in Olomouc.
- [14] AccuStandard, Inc., *EPA Methods*, [online], [26.12.2016]. Available from: <http://www.accustandard.com/asi/epa_downloads.php3>



- [15] EPA Methods, [online], [12.012.2016]. Available from: <<http://www.caslab.com/EPA-Methods/>>
- [16] FREMROVÁ, L., PITTER, P., BRÍZOVÁ, E., FRANCE, P., *Documents for the Ministry of the Environment on the implementation of the Protocol on PRTR - Review of methods of measurement and identification of substances monitored by the Protocol on the release and transfer registers in releases of pollutants into water*, Hydroprojekt CZ a.s., MŽP Praha, 2007.
- [17] FEZEKEŠOVÁ, D., *Environmental Chemistry, Part II pollutants individual components of environment*, Prešovská univerzita v Prešove, 2009, ISBN 978-80-555-0082-9, p. 255.
- [18] KOLLEROVÁ, L., et al., *Comparison of methods for the determination of dissolved fluoride, Proceedings XXXVII. "New analytical methods in water chemistry"* Hydrochémiá, Bratislava, 2006, p. 246–250.

CONTACT ADDRESS

Author: Ing. Alica Bartošová, PhD.
Workplace: Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology in Trnava,
Institute of Integrated Safety
Address: J. Bottu 25, SK-917 24 Trnava, Slovak Republic
Phone: + 421 906 068 539
E-mail: alica.bartosova@stuba.sk

Author: RNDr. Maroš Sirotiak, PhD.
Workplace: Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology in Trnava,
Institute of Integrated Safety
Address: J. Bottu 25, SK-917 24 Trnava, Slovak Republic
Phone: + 421 906 068 539
E-mail: maros.sirotiak@stuba.sk

Author: Ing. Lenka Blinová, PhD.,
Workplace: Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology in Trnava,
Institute of Integrated Safety
Address: J. Bottu 25, SK-917 24 Trnava, Slovak Republic
Phone: + 421 906 068 539
E-mail: lenka.blinova@stuba.sk