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Environmental Organic Pollutants Analyses

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Abstract

Since the main objects of environmental analyses have been inorganic compounds the interest to organic pollutants within recent 20 years increases. Organic compounds in the environment are either of natural origin or products of human activity. Their number and quantity grow rapidly and damage environment and human health. The scientists all over the world have reached an agreement about the danger of organic pollutants even in micro quantities. The environmental protection requirements lead to methods and technique elaboration. Series of analyses of drink and waste waters, atmosphere air, solid scraps, a.o. are published. The organic compounds determination is in process of permanent development. Every one analysis has a concrete method of approach; it depends on the type and concentration of the components of interest, but mostly on the staff skill level, on his ability to select the best analytical method and technique and to interpret results by the best way. Examples of modern chromatographic and analytical methods used for organic pollutants content determination in different environmental object types are given in this paper. Methods used for quantitative analyses as well as methods for isolation and identification of organic compounds are shown.

Keywords: environmental analysis, organic pollutants

1. Introduction

The industrialization has versatile effect on the population. On the one side, the profitableness and social prosperity increase, on the other - the industrial development is the main cause for human health danger either to the workmen at different production areas or to the population as a whole. The danger can be directly connected with pollutants or unsafe methods at the working places, or indirectly - by worsened quality of the environment.

The most actual world problems deal with human health worsening and premature mortality, provoked by chemical pollutants in the environment – water, air, soil and meal. Such type of environmental problems exists in the developed countries as well as in the developing ones.

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The main sources of environmental pollution are the industrial enterprises. The environmental problems settlement requires complete recognition of the number and quantity of risky compounds which can pollute different environmental sites. It is also required to understand how pollutants, their decomposition products and metabolites act in water, air, biological liquids, a.o. The first step is monitoring of different objects and their interconnecting with factors as climate, topography, working conditions, a.o.

2. Environment analyses requirements

Since the main objects of environment analyses have been inorganic compounds, the interest to organic pollutants and their metabolic products as well as to the way they influence the human life within the recent 20 years, increases. The scientists all over the world have reached an agreement about the danger of organic pollutants even in micro quantities. First the US Environmental Protection Agency (U.S.E.P.A.) followed by the European Unit, has listed the priority organic pollutants, and named them "*the black list*" in order to be tested in all environmental objects.

The basic requirement to present-day analyses of organic pollutants in environmental objects is a rapid, modern and certain methodology. The need of sensible detection, correct identification and quantitative determination of the pollutant in different concentration ranges and complex matrices is a challenge for analytical chemists. For this purpose new methods are elaborated and standardised. The methods are constantly developed and refined on the basis of technique potentialities, and increase in environmental purity requirements [1]. Each concrete analysis requires a tangible approach to the problem. Chromatography is the main technique used for testing of organic compounds in the environmental objects. The reason for this status is because chromatography combines the separation power of the method with the selectivity and sensitivity of detectors, able to fast quantitative determination. Generally, Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC) are the most utilized techniques for routine environmental analyses. Thin-layer chromatography (TLC), capillary electrophoreses (CE) and supercritical fluid chromatography (SFC) are often used as well.

In an investigation devoted to the state and the dynamics of analytical separation methods in different spheres of human activity [2] the distribution of publications discussing environmental analyses has been presented. The results are shown in Fig.1. It can be seen that chromatographic analyses are explored in 71% of all environmental analyses technique types. Spectral methods - atomic absorption (AS) and infrared spectroscopy (IR) are used in 29% of the publications referred to.

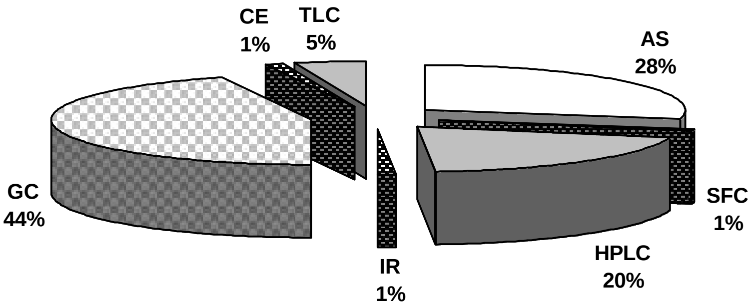

Fig. 1 Distribution of the published papers devoted to analytical separation methods in environmental analyses

In environmental analyses combined methods are usually put into practice, mainly gas chromatography-mass-spectrometry (GC/MS). The major part of EPA methods used for air and water analyses for organic compounds content determination applies this technique. Implementation of portable and ion-trap mass-spectrometers strongly influences and changes the possibility of identification by gas chromatography. The combination of high resolution with fast identification along with going down in prices of instruments turned the GC/MS to be “the working horse” in environmental analyses [3, 4]. The increase in sensitivity and selectivity, especially in the case of MS/MS with fragmentation of the first fragment, points to the mass-selective detector as the main detector in the future. In the case of specific analyses the nitrogen-phosphor detector (NPD) can be applied; for pesticides, polychlorobiphenyls, dioxins, furans - the electron-capture detector (ECD); for volatile organic compounds, aromatic hydrocarbons, etc. - the flame ionization detector (FID) [5-7]. When thermo-unstable compounds, non-volatile or high-molecular substances have to be analysed, the preferred technique is HPLC. By use of spectral, electrochemical and other detectors available the named compounds can be identified in environmental objects. The availability of detectors with diode array (DAD) increases the HPLC chances [8, 9].

Further down chromatographic techniques application is presented for environmental analyses of organic pollutants. The methods development and analyses implementation has been carried out in ”Lukoil Neftochim Bourgas”- JSC within last years. Our own authorised analytical methods are validated.

3. Air analyses

The developed method includes adsorption on activated charcoal, desorption and GC/FID analysis. Another methodology based on EPA-methods TO-1 and TO-2 was elaborated for atmosphere air analyses and industrial emissions and emissions control of volatile organic pollutants by sampling over Tenax, thermodesorption and GC/FID or GC/MS. By the mentioned methods a series of air analyses was carried out in the industrial zone and petrol tanks for fuel storage in ”Lukoil Neftochim Bourgas” as well as the neighbouring villages and Bourgas.

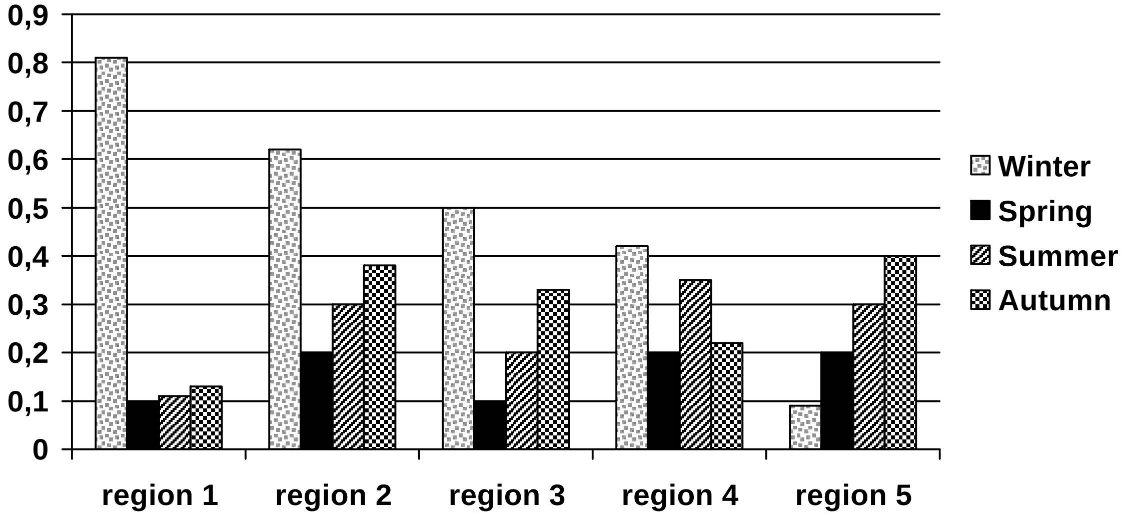

Fig. 2. Distribution of hydrocarbon pollutants in Bourgas air (mg m^{-3})

Benzene, c-hexane, toluene, ethylbenzene, xylenes, styrene, i-propylbenzene, naphthalene and total hydrocarbons were determined. The analyses were carried out during four seasons; the results were correlated with meteorological data of the controlled period (wind speed and course, temperature, a.o.) [10]. One example referring to the mentioned investigation of the total content of volatile hydrocarbons in Bourgas city air is presented in Fig.2. The region 1–5 is housing estates (1 and 2 between the plant and the city, 3 and 5 along the sea, 4 – in city centre. The limited permissible concentration according to Bulgarian standards is 1.5 mg m^{-3}. Fig. 2 presents the emissions (mg m^{-3}) from fuel tanks – gas oil and diesel. The emission examination includes also measuring of mass flow (kg h^{-1}). An exception in this particular example is the benzene content; the other values are below the limited standards.

The quantity and distribution of the carbonyl compounds in the atmosphere is related to photochemical processes, but may also be due to anthropogenic influence - incinerators, car exhausts, a.o.

Notwithstanding the special significance of carbonyl compounds, their distribution in time and space is still not very clear. Data collection of aldehyde concentration changes per days and per seasons is required. These data may be used for mathematical modelling of photochemical generation of ozone and other oxidants, more harmful substances than the aldehydes.

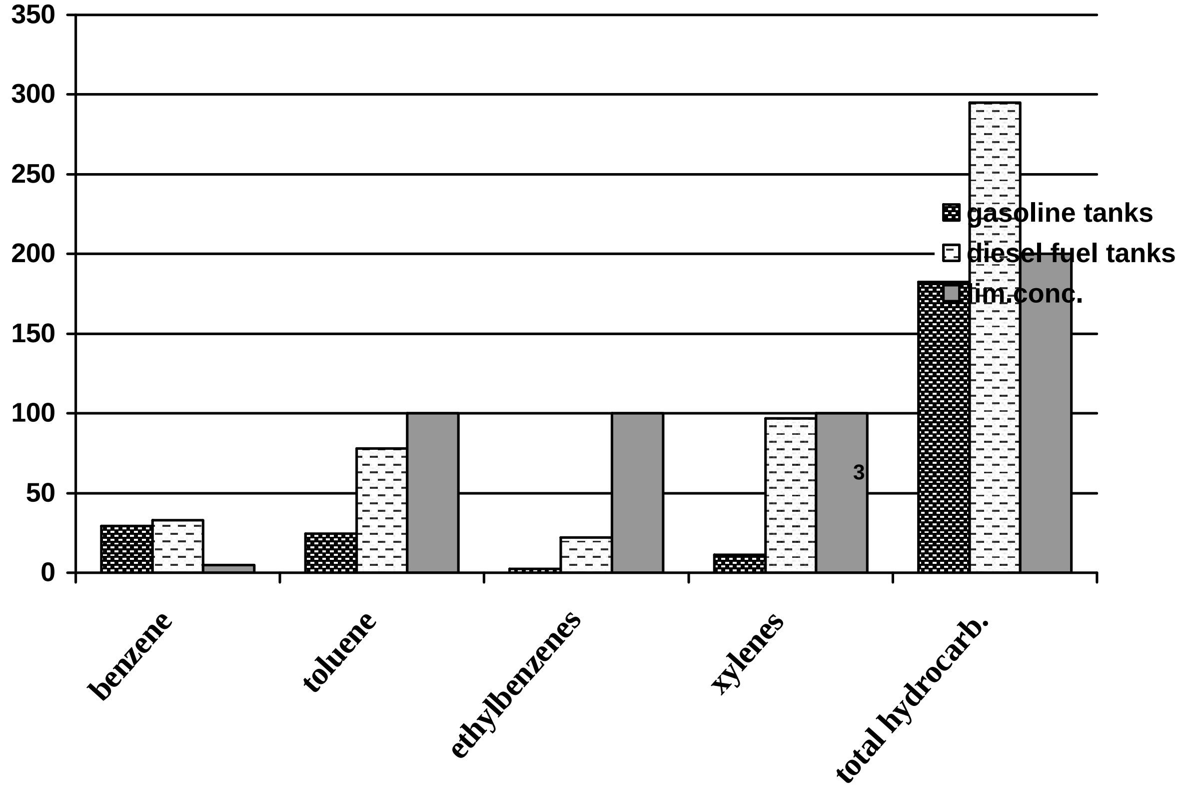

Fig. 3. Emissions of volatile organic pollutants , mg m-3, from fuel tanks

An analytical method for detection of 13 carbonyl compounds was developed. The named compounds are specified by EPA as priority organic pollutants. The method is based on TO-11; HPLC is used for preconcentration and derivatization of carbonyl compounds. The region of “Lukoil Neftochim Bourgas” plant area, built – up areas and settlements around the plant, the city of Bourgas, some industrial objects in the named region were tested for carbonyl compounds concentrations [11].

Some data of the carbonyl amount measurements in different regions of Bourgas in 2000 are shown in Fig.4. The data are the average values for a period of 12 months monitoring. The city points 1 and 2 on Fig.4 are the regions of high loading with urban transport. Point 3 is the park along the sea of Bourgas; point 4 is a seaside housing estate place and point 5 – a city complex close to the industrial zone. The limits of the acceptable concentrations are: 0.1 mg m^{-3} for formaldehyde, 0.01 mg m^{-3} for acetaldehyde, and 0.35 mg m^{-3} for acetone.

It can be seen, that the concentrations of acetaldehyde exceed the acceptable limited values. The highest acetaldehyde contents are detected in the second region (point 2); the region with the highest concentration of total carbonyl content is the first spot (point 1).

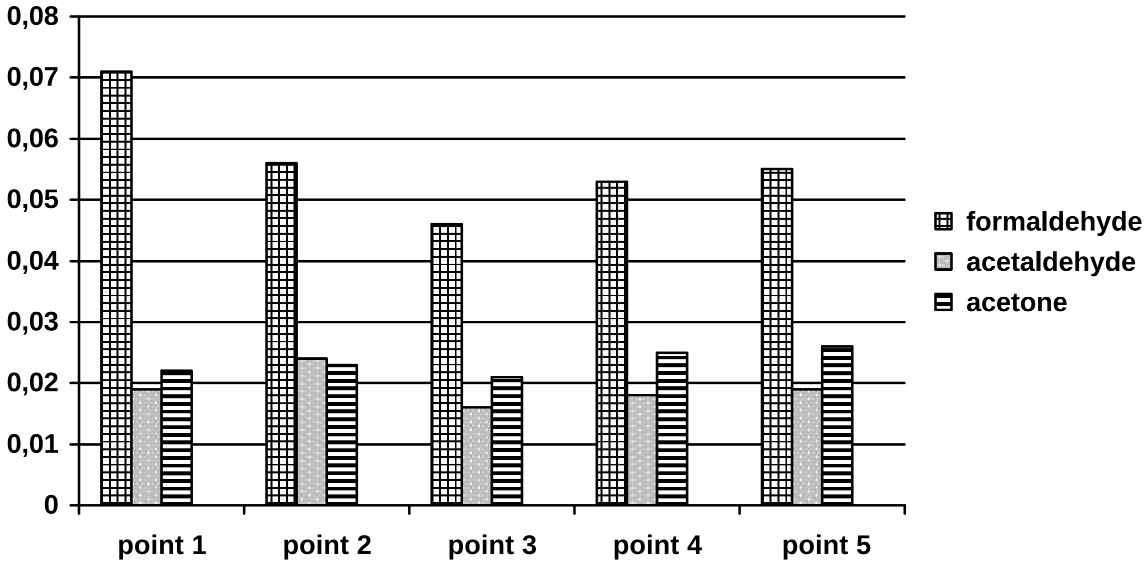

Fig. 4. Average values of carbonyl compound concentrations (mg m-3) in the atmosphere of Bourgas city

4. Water analyses

Determination of organic compounds in waters (waste and drink) is always connected with preliminary extraction and preconcentration. When the analyte concentrations are in ppb, the analyses are complicated both in procedure and accuracy.

Methods were developed for determination of volatile organic compounds (VOCs) by head-space (HS) and solid-phase extraction (SPE) followed by capillary GC/FID [12]. In Table 1 the accuracy values of the methods for aromatic hydrocarbons determination according to validation requirements are presented. Precision and accuracy of both methods are comparable and satisfactory. HS-GC method is faster, the limit of quantitation of HS-GC is 3 ppb and that of SPE-GC is 1.5 ppb.

Which method should be preferred, depends on equipment available, sample amount, sensitivity required, sample matrices, a.o. The developed methods were applied to determination of the biodegradation of aromatic compounds in water and for analyses of clean waters.

Table 1 –Validation parameters of the HS-GC and SPE-GC methods.

			Reproducibility					
	Range, ppb		**SD, (ppb) *(%)***		**RSD, (%)**		***Bias***	
Compounds	HS	SPE	HS	SPE	HS	SPE	HS	SPE
Benzene	5-15	-	0,53	-	5,8	-	9,8	-
Toluene	5-15	2-15	0,52	0,35	5,5	4,1	7,8	3,4
Ethylbenzene	5-15	2-15	0,52	0,29	5,6	3,4	3,0	8,0
p-Xylene	5-15	2-15	0,68	0,34	6,8	3,9	2,0	4,6
o-Xylene	5-15	2-15	0,67	0,32	6,7	3,8	2,0	3,4
Isopropyl-benzene	5-15	2-15	0,70	0,36	7,0	4,1	3,9	4,6
Recovery, %	HS 94,3-100,8	SPE 91,4-96,8						

Other methods were developed for GC analysis of waste and purified industrial waters. For sample preparation different techniques are used like liquid-liquid extraction (LLE), SPE and HS. The detection of organic compounds in waters is performed with FID and mass-selective detector.

A method of chlorophenols determination by SPE and HPLC with UV-detection and DAD was developed. The method includes the identification of 11 phenols, specified by US EPA as priority pollutants in water [13]. As a tool for preliminary sample preconcentration two methods were tested and compared – LLE and SPE. The solid-phase approach yields higher recovery. The method was applied for determination of individual chlorophenols in purified waste waters, as well as in sea, river and drink waters. The method's accuracy complies with the requirements.

Methods were developed for investigation of spill oils in sea water [14]. While developing the methods and making differentiations between fresh and old oil spots we have elaborated a block diagram for tracing the contaminant. Software for chemometric approach was worked out.

The approach was exploited for identification of eight types of petroleum and four types of diesel engine fuels. It was successfully applied to the detection of sources of real environmental accidents in Bourgas bay as well.

5. Polluted soils and bottom sediments analyses

Soil pollution with hydrocarbons and subsequent land purification is one of the largest environmental and industrial problems. The pollutants determinations are difficult because organic compounds are originally present in soils.

Original laboratory methodologies were developed for the analyses of soil polluted with petrol and petrochemical products, for determination of the distribution of n-alkanes and isoprenoids in soils polluted with diesel fuel. The methods include extraction, purification, preconcentration and analysis with GC/FID, as well as finding of characteristic parameters, the bearers of information about the changes in fuels content as a function of time and meteorological influences. Such investigations are used in order to check the changes during the process of soil remediation, to elaborate the cleaning procedures and to distinct the soil infection compounds from the original components [15].

Polycyclic aromatic hydrocarbons (PAH) are widely spread in all environmental objects. Many of them are known to be with cancerous and /or mutagenic effects.

Methods were developed for PAH detection in air and waters (GC/FID and GC/MS) and a method for determination of 16 PAH in soils and bottom sedimentations. Methods and techniques used include drying, extraction and preconcentration, followed by liquid chromatography and HPLC/UV detection with DAD. The achieved values of minimum determined concentrations are comparable with standard values [16].

The methods are applied to air, waters, soils, bottom sediments and other analyses.

The obtained data from implemented investigations and monitoring are used for making of manager and government decisions to eliminate and/or reduce pollutants and improve environmental situation.

6. Biologic liquids analyses

Toxic solutes damage and corrupt the living beings. The need of precise and high-sensitive analytical methods for their detection in biological medium – blood, urine and breathing out air increases incessantly. It is closely connected with the extremely high requirements to effective biomonitoring on the one side and a possibility for taking quick decisions at incidents, poisons, etc. – on the other.

The approach in this field includes the determination of the main air pollutants in the region, working area, etc., the analytical method development for analyses of toxic compounds and /or their metabolites in biological samples (blood, urine), the adoption of the analytic techniques and procedures of biological sample preparation, and the organizing of toxicological analyses of staff working in dangerous for health conditions.

Determination methods of phenol, almond acid, phenylglyoxalic and hypuric acids in urine (metabolic products of benzene, styrene, ethyleneglycol, aromatic hydrocarbons and other pollutants in air) have been developed [17]. The techniques used are extraction, salting out, derivatization, and quantitative analysis by HS-GC.

A method for determination of phenol, acrylonitrile, acetone and volatile organic compounds in blood with HS-GC was developed [18]. The method’s sensitivity was increased by using different techniques for registration and determination of solute quantities below their reference values. The method is applied to urgent toxicological analyses of persons exposed to damages, incidents and chronic intoxications.

Methods were developed for determination of *tr-tr*-muconic acid, acrylonitrile, acetone and volatile aromatic hydrocarbons in urine; of o-cresol in urine (specific biomarker for toluene); of 2-,3- and 4-methylhypuric acids (specific biomarkers for o-, m- and p-xylenes) by HS-GC and HPLC.

The data from investigations of workers are treated by a developed program to report the results individually and by professions. An evaluation of the influence of the chemical factor of the working climate upon different professional groups was done.

7. Retention modelling

A great variety of methods and techniques was used for identification of organic compounds in environmental analyses. Side by side with conventional analytical methods, theoretical methods based on Quantitative Structure-retention relationships (QSRR) correlations are proposed. Multiple linear regressions [19, 20] are the statistical method most frequently used in QSRR studies. For the series of 21 substituted phenols including priority pollutants, separated in HPLC by isocratic elution [21] in polar eluent mixture, the retention was modeled by the QSRR approach [22]. Linear multi-parametric regressions were derived in the form of equation (1):

$K'_{rp} = a_0 + dD + \sum p_i P_i$ (1)

Where K'_{rp} is capacity factor; D – global molecular index – the descriptor of dispersive intermolecular interactions between the solutes and the chromatographic phases, P_i – local molecular descriptor (polar descriptors). Wide range of global and local molecular indices were calculated and used as descriptors for regression deriving. Multiple linear regressions include one global calculated molecular index (the molar refraction in the case) and some indicative structure descriptors:

$\mathbf{K'_{rp}} = -37.78(\pm 3.10) + 1.11(\pm 0.08)\mathbf{MR} - 0.55(\pm 0.54)\mathbf{Cl_{ortho}} - 2.59(\pm 0.97)\mathbf{Cl_{para}} - 5.18(\pm 1.24)\mathbf{NO_{2\,orhto}} - 4.48\ (\pm 1.17)\mathbf{NO_{2\,para.}}$;

$(n=21;\ R=0.980;\ R^2=0.960;\ s=1.42)$

The descriptors $\mathbf{Cl_{orto}}$ and $\mathbf{Cl_{para}}$ indicate the presence of Cl-substitution in *ortho*-, (or *para*-) position in the solutes; respectively the descriptors $\mathbf{-NO_{2\,ortho}}$ and $\mathbf{-NO_{2\,para}}$ reflect the presence of a nitrogroup in the solute structure. The equations derived have the adequate precision.

If the quantitative relationships between the retention data as dependent variables and the numerically expressed solute properties are precise enough, they can be used for the retention prediction of the given set of solutes separated under the given chromatographic conditions.

8. Conclusions

The world's attention to the danger of organic pollutants in the environment increases and leads to development of analytical methods for their determination. Current methods and techniques provide the needed sensitivity, selectivity, accuracy and precision. For the recovery and preconcentration, LLE and SPE are the techniques most frequently used, while for determination GC/FID, GC/MS and HPLC/UV are the most widely employed methods. When a standard and/or laboratory's own method is used, a set of quality control measures should be included to evaluate and document the quality of data.

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