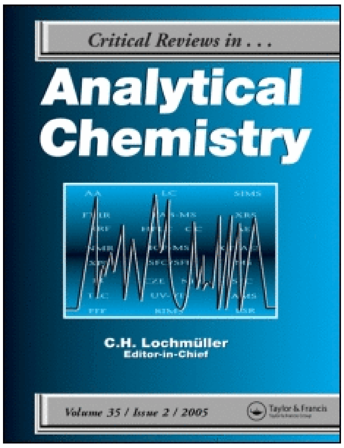

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Magdalena Rawa-Adkonis[a]; Lidia Wolska[a]; Jacek Namieśnik[a]
[a] Department of Analytical Chemistry, Chemical Faculty, Gdańsk University of Technology (GUT), Gdańsk, Poland

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Analytical Procedures for PAH and PCB Determination in Water Samples—Error Sources

Magdalena Rawa-Adkonis, Lidia Wolska, and Jacek Namieśnik
Department of Analytical Chemistry, Chemical Faculty, Gdańsk University of Technology (GUT), Gdańsk, Poland

Today, special attention is paid in environmental analysis to sample preparation methods. Isolation and/or preconcentration of analytes from water samples characterized by complex composition of the matrices constitutes an essential step of analytical procedures used for determination of trace organic components. Collection, transport and storage of water samples are also important. This review paper systematizes available information connected with the occurrence and the analysis of PAHs and PCBs in natural waters. Special attention is paid to point out error sources, which can appear in every step of the analytical procedures.

Keywords water analysis, PAHs, PCBs, techniques of extraction

INTRODUCTION

The fact that the opinion of the environment's constant deterioration is nowadays generally accepted makes state and local government authorities, and some other institutions, take initiatives and activities to reduce the negative effects of civilization development. The effectiveness of environment management strongly depends on availability of information on environmental quality and processes. The basic sources of information are environmental monitoring and scientific studies (1–3).

Correctness of analytical data results from the reliability of the analytical procedures and the measuring systems used. The modern analytical procedures should be characterized by:

- low detection limits for possibly wide spectrum of the compounds analyzed;
- lack of interference and minimum artifacts;
- traceability assurance by the application of reference materials;
- ability to identify all sources of errors and to determine *budget of uncertainty*.

The important area of modern environmental analytics is determination of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), which are highly toxic and mutagenic and environmentally common and persistent (4–8). Not surprisingly these pollutants are on U.S. EPA (Environmental Protection Agency) list of priority pollutants. That analytics of PAHs and PCBs are of high importance can be evidenced by the large number of reviews and original papers published every year, which deal with problems of their determination and new methodological and instrumental developments to combat the problems.

Until recent times, analytical chemists' attention was drawn to accuracy and precision of final determination, whereas the steps preceding the final analysis such as sampling, transport, storage, preservation as well as isolation and enrichment influence reliability of analytical results to a high degree (9, 10).

These stages of analysis are very significant in analysis of PAHs and PCBs in water samples. The compounds are hydrophobic, of low volatility and have a high tendency to undergo adsorption on solid particles (suspended matter), glassware and devices for sample collection and storage. Moreover, the compounds are sparingly soluble in water; and therefore they are present in aqueous phase on trace level. The problems of trace analysis of PAHs and PCBs were comprehensively described in the rather large review by Nameśnik (1).

SAMPLE COLLECTION, TRANSPORT AND STORAGE

Processes of sample collection, transport and storage should be performed is such are way that samples remain in unchanged form until they are subjected to final analysis. The main processes deteriorating sample integrity are:

- physical processes, mainly analyte adsorption on the walls of samplers and vessels used and also evaporation of volatile components;

Address correspondence to Magdalena Rawa-Adkonis, Department of Analytical Chemistry, Chemical Faculty, Gdańsk University of Technology, 11/12 G. Narutowicz Street, Gdańsk 80-952, Poland. E-mail: chemanal@pg.gda.pl

- chemical reactions (e.g., oxidation, reduction, complexing);
- biological reactions (e.g., photolysis, biodegradation) (1, 2).

To minimize these negative effects, the analysis should performed without delay, i.e., the time between sampling and final analysis should be as short as possible, and appropriate methods of sampling, conservation, transport and storage should be applied.

Reviewing technical standards of water sample collection for PAHs and PCBs determination the following recommendations can be found (8, 11–17).

1. vessels and devices for water sampling should be made of such materials as PTFE, stainless steel, borosilicate glass (without using grease and oil);
2. the use of vessels, connectors and tubing made of polypropylene or polyethylene (this is common) can be a source of errors caused by:
    - elution of plastifiers;
    - entrance of analytes into material pores;
    - growth and gathering of bacteria on material surface, which can intensify processes of biodegradation of analytes.
3. when large water samples are to be collected pumping systems that allow sampling at high depth and in-site extraction systems for handling large samples (e.g., on board of research ships) should be applied (18);
4. samples should be stored at temperature of +4°C for up to 24 hours (up to 72 hours with hexane addition) (19) or up to 96 hours at −20°C in stainless steel containers. However, solvent extracts or sorption tubes with analytes trapped can be stored as long as one month in a freezer in glass vials closed with PTFE stoppers (12). Storage at −20°C decreases the risk of loss of PAH and PCB analytes due to a decrease in microorganisms' activity, but it can intensify processes of adsorption of trace components on container surfaces.

Despite the fact that great attention is paid to selection of materials that have contact with samples, the most common use of PTFE appeared to be a wrong choice. It was shown that 40–80% of PCBs could be sorbed on PTFE surface (20). This was confirmed in later papers as well (21). The papers dealing with PAH determination suggest that the loss of analytes is caused by sorption on particular elements of the system (11, 22). Unpublished studies of the authors show that 10–60% analytes can be sorbed on glass surface. It was confirmed that adsorption on glass can be responsible for 10–25% loss of PAHs and PCBs (6).

All this suggests that it is difficult to show which material should be used to collect and store water samples for PAH and PCB analysis. An additional problem results from the presence of particulate matter in water samples. Due to low volatility and hydrophobic character, PAHs and PCBs have a tendency to adsorb on large and colloidal size particles, and to interact with molecules of humic and fulvic acids, proteins and fats dissolved in water (23). The studies prove that presence of suspended matter can lead to 20–70% loss of PAHs during transport and storage (24). Many years' literature studies suggest that the knowledge on the scale of loss of PAHs and PCBs during sampling, transport and storage is incomplete in spite of the fact that scientists are conscious of the possibility of loss.

ISOLATION AND ENRICHMENT

In analytical practice, a wide spectrum of techniques of isolation and enrichment of PCBs and PAHs is used. The general classification of the techniques is schematically presented in Figure 1.

Liquid-Liquid Extraction—LLE

Liquid-liquid extraction (LLE) is one of the oldest methods used for isolation of organic compounds from water. The technique is based on analytes' partitions between organic solvent and aqueous solution. Many papers have been published that describe determination of PAHs and PCBs with the use of LLE. The technique gives excellent results (recoveries are on the level of 100%). Despite these high recoveries, LLE is thought to have many shortcomings (Table 1) (25–27).

Pursuit of diminishing disadvantages of the technique resulted in proposition of many new approaches:

- Microscale Solvent Extraction—MSE (28);
- Single Drop Microextraction—SDE (29);
- Gulden Large Sample Extraction—GLSE: a stream of an aqueous sample flows through a vessel filled with solvent heavier than water, mixing is very efficient (10);
- Continuous Liquid-Liquid Extraction—CLLE (26).

TABLE 1
Advantages and shortcomings of LLE in isolation of analytes from aqueous samples

Advantages	Disadvantages
• Methodological simplicity • Simple apparatus	• Labor-intensive • Consumption of large quantities of high purity solvents; this is very hazardous for environment since environmental pollution increases • Often low enrichment factor • Low selectivity • Possible formation of emulsion • Problems with handling of large sample volumes

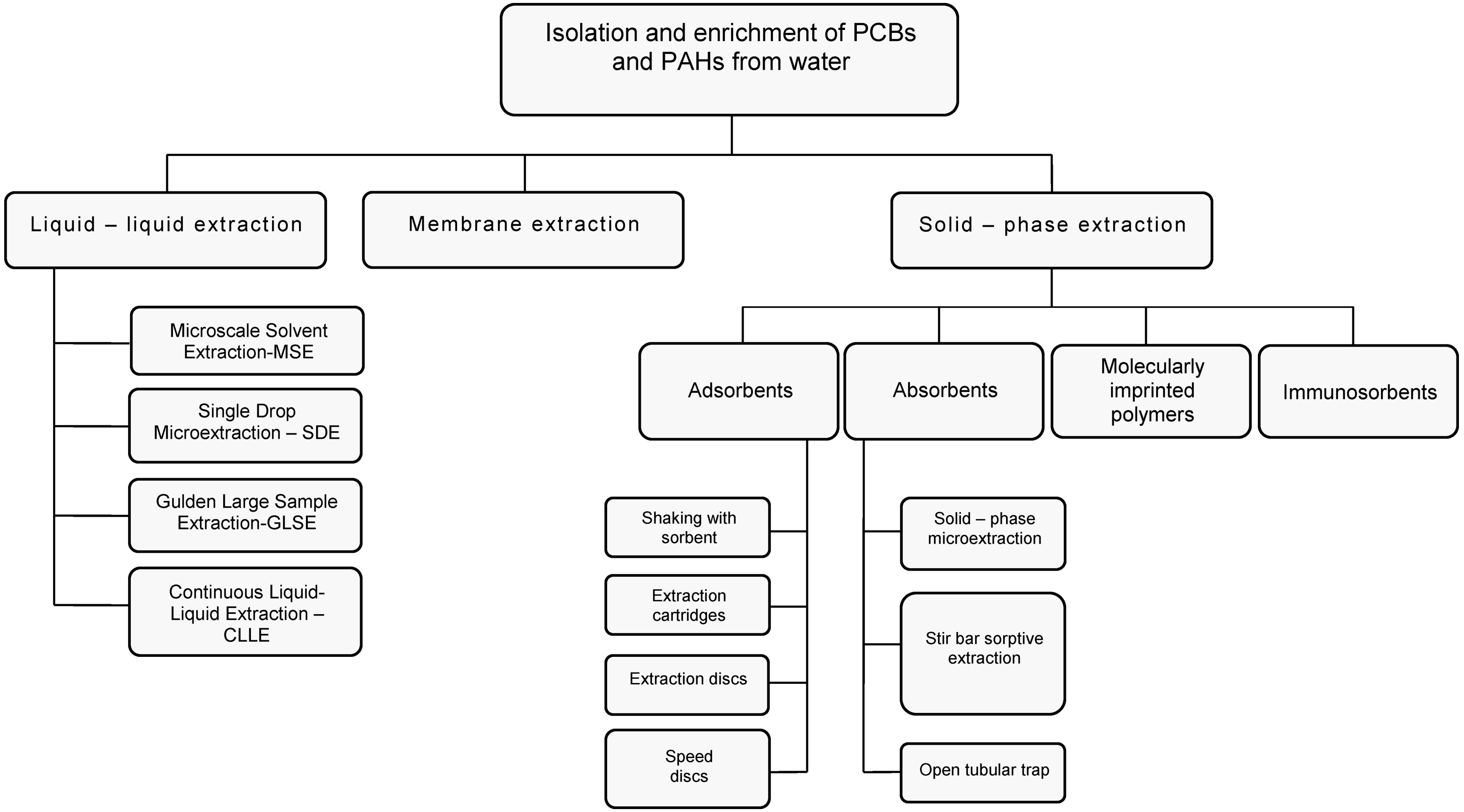

FIG. 1. Techniques of isolation and enrichment of PCBs and PAHs from water.

Solid Phase Extraction—SPE

In solid phase extraction (SPE) an organic analyte partitions between a liquid phase (the sample studied) and solid phase (sorbent), resulting in selective trapping of analytes on sorbent.

The contact of sample with sorbent can be achieved in the following ways:

- shaking sample with sorbent;
- percolation of sample through extraction cartridges packed with sorbent (e.g., silica gel most often modified with octyl or octadecyl groups) (6, 30–34);
- passing the stream of sample through so-called Empore Disks—ED (34);
- passing the stream of sample through so-called Speed Disk—SD (34, 35);
- similar to LLE, SPE has been dealt with comprehensively in scientific journals (30, 32, 35, 36).

Great attention is paid to appropriate sorbent selection, sorbent conditioning, and choice of solvent for analyte elution from sorbent bed (34).

Recoveries of PAHs and PCBs in SPE-based procedures are on the level of 70–100%, and 50–70%, respectively. The studies were conducted with the use of model solutions and the results are limited to the steps of isolation, elution and enrichment of analytes. In these papers, detailed descriptions of model solution preparation are generally not given (standards addition to water—the solvent applied, possible agitation and the time length between standards addition and isolation). Model solution preparation can have a significant effect on the degree of analyte adsorption on surface of extraction apparatus, which can lead to different recoveries. It seems that the recoveries published are only for the process of isolation and not for the whole procedure. Advantages and disadvantages of SPE technique are presented in Table 2 (37, 38).

TABLE 2
Advantages and disadvantages of SPE technique in isolation of analytes from aqueous samples

Advantages	Disadvantages
• Possibility of storage of analytes enriched on solid sorbent (analytes on the sorbent can be transported and stored, which permits us to carry out analysis at a suitable time and under suitable conditions) • Possibility of isolation of analytes of medium and low volatility • Reduced consumption of toxic solvents • No problems with emulsion formation • Enrichment factors higher than in LLE • Easiness of process automation	• Possibility of low recoveries due to interaction between sorbent and sample matrix, or to exceeding breakthrough volume • Sometimes low reproducibility due to differences between sorbent batches • Sorbent bed clogging (cartridges as well as disks) by particles of sample suspended matter

The disadvantages of the SPE technique noted here are mainly related to sorbent properties. The traditional sorbents used in SPE are not sufficiently selective, and therefore some matrix components can be trapped simultaneously with analytes. A very promising variety of SPE technique is Dynamic Ion Exange-Solid Phase Extraction (DIE-SPE). In this approach the disadvantageous effect of humic acids is eliminated. It was found that the application of RP-18 sorbent in DIE-SPE gives higher recoveries of 5- and 6-ring PAHs than when classical SPE is used (39).

Inconveniences of the classical sorbents used have led to a search for new types of sorption materials—this resulted in polymer sorbents that are inherently homogeneous and do not have pores. Analytes are trapped by these sorbents due to the process of solution in the sorbent and not due to surface adsorption. The fact that the sorbents are inert materials decreases the risk of loss of unstable or polar compounds caused by irreversible adsorption or catalytic reactions. The most often used material of this type is polydimetylosiloxane (PDMS) (40). For more polar analytes polybutylacrylate is recommended.

New absorption materials, as well as different methods of their coating on solids, resulted in development of the following techniques that in fact are modifications of classical SPE (41):

1. Solid-phase microextraction;
2. Stir bar sorptive extraction;
3. Open-tubular trapping.

Solid-Phase Microextraction—SPME. Sorbent film (liquid stationary phase or adsorbent) is coated on the surface of thin glass or fused silica fibers (42, 43).

PME is simple and fast, its applicability is limited, due to small amount of polydimethylsiloxane, and hence small process effectiveness. In the final analysis, selective or even highly specific detectors must be used. There are many papers describing PAH and PCB determination in water samples based on the technique (44–54). However, the results are not encouraging. Recoveries are generally low, especially for high-boiling PAHs. Authors do not give the source of the fact. Taking into account that the process lasts 60 minutes, it can be thought that one of the causes can be adsorption on the wall of the vessel containing a sample. Significantly higher recoveries on the level of 60–100% were obtained for PCBs by combining SPME with headspace (HS) and microwave-assisted extraction (55).

Sorbent capacity can be increased by using such mixed phases as PDMS-divinylbenzene (PDMS-DVB), PDMS-Carbowax

TABLE 3
Advantages and drawbacks of solid phase microextraction of analytes from aqueous samples

Advantages	Disadvantages
• Solvent elimination • Short analysis time • Simple analysis conducting and maintenance • Low analysis cost • Easiness of automation	• Sensitivity of PDMS-coated fiber to presence of suspended matter • Sorption processes of analytes on fiber compete with analytes' sorption on suspended matter surface • Low effectiveness of process due to small amount of PDMS coated on fiber

(PDMS-WAX), and PDMS-Carboxen (28). However, the polymers added remain active for only a short time; analytes must compete for adsorption sites with humic acids and their salts (40). Table 3 presents advantages and drawbacks of SPME (43, 56, 57).

Stir Bar Sorptive Extraction. In 1999, a research group of Prof. P. Sandra proposed SPE in which a moving agitation bar is used as a trapping element; this variety of SPE is called Stir Bar Sorptive Extraction (SBSE). The larger amount of SPME coated on a bar makes the isolation process more effective and ensures higher recoveries (48, 51). After isolation, the stirring bar is taken out of the sample; sorbates are desorbed thermally or with solvent and determined by one of chromatographic techniques (31, 32, 48, 51, 58, 59). Though the technique is relatively new, there are quite a few papers where it is used for determination of medium- and high-boiling compounds in water samples (20, 31, 32, 40, 48, 49, 51, 58, 59).

Open-Tubular Trapping—OTT. In this technique, short lengths of Wall Coated Open Tubular (WCOT) and Support Coated Open Tubular (SCOT) gas chromatographic columns are used. WCOT is a GC column of small diameter whose wall is coated with thin film of liquid stationary phase and SCOT is a GC column of small diameter whose wall is coated with a solid support coated with thin film of liquid stationary phase (60–63).

Until now, only a limited number of papers have been published where short lengths of capillary columns were used for isolation of PAHs and PCBs from water samples (64, 65). Applying a multiple sorption the recovery on the level of 60% was obtained (66). Here we described modifications of classical SPE taking into account a way in which sorption material (PDMS) is coated on support. It should be also mentioned that new sorption materials are available which permit to avoid problems appearing when classical sorbents are used. They are immunosorbents and Molecularly Imprinted Polymers (MIP).

Immunoextraction is based on the use of antigens immobilized on appropriate supports. They are immunosorbents, very selective sorbents for SPE used to combat problems encountered in the case of non-specific sorbents. Intensive research is done in the area of Enzyme Immunoassay (EIA), whose modification is double antibody sandwich technique known as Enzyme Linked Immunosorbent Assay (ELISA) (41, 67, 68). The use of the technique for isolation and determination of PAHs and PCBs in aqueous samples can be found in literature (68–70). Comparison of the results of determination of PAHs in river water obtained with ELISA and conventional GC-MS techniques, shows that ELISA values are, usually higher than those reported for GC-MS (68).

It should be remembered, however, that preparation of immunosorbents used in immunoanalysis is difficult and expensive. These limitations led to further research aimed at synthesis of sorbents recognizing a substance of interest (analyte)—this is called *molecular recognition*. A technique based on the use of highly cross-linked polymers with imprinted sites interacting with analyte molecules (molecular imprinting) is called Molecularly Imprinted Solid Phase Extraction (MISPE). It is mainly used in determination of pesticides, phenols, aminoacids and medicines (71–73). There are some reports on attempts to use these sorbents for isolation of PAHs (70).

Membrane Extraction

For isolation of organic compounds from water, permeation or transfer of the compounds through semi-permeable membranes made of silicone rubber, low density polyethylene (LDPE), PTFE, etc. have been used for many years. Analytes that pass through the membrane are taken in by acceptor medium (a stream of gas, solvent or sorbent). They can be transported directly to a measuring device. A spectacular application of membrane extraction for determination of volatile organic compounds is direct coupling of the device with ionization chamber of mass spectrometer (Membrane Introduced-Mass Spectrometer (MIMS) (10, 41).

There are many applications of membrane extraction in determination of PAHs and PCBs (73–75). The effectiveness of extraction depends on membrane type, physico-chemical characteristics of analytes, time and condition of extractions. Using polypropylene membrane in determination of PCBs in water, recoveries of 40–80% were obtained at an elevated temperature of 45°C.

SUMMARY

Table 4 presents main sources and their characteristics of analytical problems affecting the quality of the results of determination of PAHs and PCBs in water sample. It seems that the main sources of errors are hydrophobic nature as well as volatility of PAHs and PCBs. This results in sorption of the analytes on

TABLE 4
Characteristics of problems of PAHs and PCBs determination in aqueous samples

Source of problem	Description	Analytical problems
Physicochemical characteristics of PAHs and PCBs		
Volatility	PAHs and PCBs are generally low volatile substances, differences in volatility between particular members of each group are quite large (PAH: naphalen $T_{bp} = 218°C$, vapour $pressure_{25°C} = 0.05$ mm Hg; benzo(g,h,l)perylen: $T_{bp} = 550°C$, vapour $pressure_{25°C} = 1.03 \times 10^{-10}$ mm Hg, PCB: monochloro: $T_{bp} = 278°C$, vapour $pressure_{25°C} = 16.5$mm Hg; PCB180: $T_{bp} = 480°C$, vapour $pressure_{25°C} = 4.2 \times 10^{-3}$ mm Hg)	Loss of more volatile analytes during sample storage and transfer to appropriate vessels as well as in such operations as evaporation to reduce volume or exchange solvents
Hydrophobicity	PAHs and PCBs are apolar; logarithm of octanol-water partition coefficient is in the range of 3.3–6.6 and 5.6–8.4 for PAHs and PCBs, respectively	Differentiated adsorption of analytes on devices walls used to collect, transport and store water samples and to isolate and/or enrich analytes
Biodegradation and photodegradation		
Presence of microorganisms in sample	Commonly accepted hypotheses of biodegradation of organic compounds assume that bacteria consume only substances dissolved in the aqueous phase. In the literature, information can be found that biodegradation is faster in the presence of suspended matter and humic substances. Low solubility of PAHs and PCBs is responsible for easy biodegradation half-time for biodegradation are 3–16 days for PAHs and 2–3 much longer for PCBs (biodegradation decreases with increasing degree of chlorination)	Loss of analytes resulting from micro-organisms activity is difficult to assess
Radiation	Photodegradation is a chemical reaction that occurs in compounds under the influence of photons or light. In an aquatic environment, the processes of direct and indirect photolysis occur concurrently. Microorganisms and sediment particles suspended in water cause the dispersion of light and, therefore, can be a certain barrier for the light penetrating deeper water layers.	Loss of analytes resulting from irradiation activity is difficult to assess
Presence of suspended matter, humus, high molecular substances and other mater		
Presence of suspended matter (organic and inorganic particles)	Due to hydrophobic nature, PAHs and PCBs, show a high tendency to adsorb on suspended matter. Enrichment factors are on the order of 10^6 for PAHs and 10^3 for PCBs	High and differentiated losses of analytes resulting from adsorption on suspended matter during transport, storage and isolation Problems of sample representativeness Technical problems related to SPE cartridges clogging
High molecular and other substance	Due to hydrophobic nature, PAHs and PCBs show high tendency to interact with high molecular substances, the degree of sorption is not know	Differentiated and difficult to asses loss of analytes resulting from interaction with large molecules present in dissolved phase of natural waters Technical problems related to emulsion formation

vessel walls and parts of devices used in analytical procedures mainly during sampling, transport and isolation of analytes, and also sorption on suspended particulate matter present in natural waters. The effects intensity varies from compound to compound in each group. It is estimated that major quantity of these analytes undergoes these processes. The loss of analytes can reach as much as 80–90% of the initial amount of the least volatile analytes.

Taking this into account, one can expect that quality assurance of analytical results for the analytes in water samples is not an easy task. The problem becomes more difficult to combat because appropriate certified reference materials, which can be used in analytical practice are not available. This makes it impossible to control and estimate loss of analytes during sampling water and sample introduction into vessels for transport and storage.

Efficiency of successive steps of the analytical procedure of PAH and PCB determination is usually characterized by recovery. The recovery is determined in model studies where model samples are analysed. The samples are obtained by adding methanolic standard solutions of analytes to analytes free water. Amounts of solution should be added such that solubility of analytes in the mode sample is not exceeded.

In such solution, immediately after standard addition, does the process of analytes adsorption on the vessel wall start. Analytes are isolated from such a model sample by means of solid phase-extraction (SPE); then the results will depend on the time of contact of the model sample with vessel wall before an isolation step and the time of operation itself.

The problem will not be combatted by isopropanol addition that is used in many analytical procedures to reduce sorption on wall surface. Therefore the use of surrogate standard addition is usually recommended in procedures of PAH and PCB determination. Isotopically labeled standards, and PCB 30 and PCB209 are generally used in the case of PAH and PCB, respectively. Do really such procedures give real recoveries? The answer to this question is not easy, because surrogate standards reflect the fate of analytes in the sample only from the moment of their introduction. It should also not be forgotten that natural forms of the analytes in water samples (result of solvation, association with other compounds present in water, possible adsorption on suspended matter) can be different from standards introduced into water in a form of solution in solvent. Odds are that the problems related to sorption on vessel wall surface and parts of the devices used for isolation processes do not appear in liquid-liquid extraction that is still routinely used in many laboratories. None of the methods until now used for PAH and PCB isolation from water (SPE and LLE). Gives speciation of the analytes in water ecosystem (environment). The occurrence of suspended matter in the water sample can significantly influence the quality of final results.

Taking all this into account it seems that development of techniques of isolation of PAHs and PCBs from water should be aimed at solving these two problems, i.e., effect of analytes adsorption on quality of the results and possibility of speciation in natural waters. Simultaneously with testing reliability of the methods presently used and the proposed modifications and improvements, the analytical chemists concentrate on development of:

- new analytical procedures enabling quantitative determination of analytes directly in the medium studied in a real time (with no sample pretreatment), e.g., with the use of laser induced time-resolve fluorescence (11);
- kits for in situ determination of PAHs and PCBs analytes in water using immunoanalysis;
- specific sorbents of the molecularly imprinted polymers type that make enables specific trapping and liberation (before the final analysis) given analytes; this in turn, can enable development of a new generation of fit for purpose analytical procedures.

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