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SAMPLE TREATMENT TECHNIQUES FOR ORGANIC TRACE ANALYSIS

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Abstract - Sample preparation techniques include all steps from sampling till the final separation/determination procedure. Control of contamination of labware, chemicals and solvents is the fundamental requirement in organic trace analysis, particularly in the case of environmental samples. Sampling is often connected with enrichment, in this case the efficiency has to be determined. Metal and glass are the preferable container materials for sampling, storage and handling in trace analysis of organic compounds. General aspects of separation of the compounds of interest from the bulk of the matrix are discussed for air, water, solids, and biological materials. Specific aspects of sample treatment and group separations are discussed for aliphatic (C_8 - C_{40}) and aromatic hydrocarbons, volatile halocarbons (Freons - hexachlorobenzene), polychlorobiphenyls (PCB), chlorinated pesticides including the polychlorocamphenes (Toxaphene), polychlorodibenzofurans (PCDF), and polychlorodibenzodioxins (PCDD).

INTRODUCTION

Sample treatment techniques for organic trace analysis basically follow the same principle as for the trace analysis of the elements. Reduction and control of blank signals of whatever origin and the separation of the compounds of interest from the matrix are the major steps. Sampling, as the initial step of the analytical procedure, is of major importance in trace analysis, though this importance is often overlooked or neglected. The sampling step itself as well as transport and storage of the samples all have to be integrated in the sample treatment strategy otherwise severe systematic errors may occur [1-15].

Sample treatment techniques will be discussed from the sampling till the injection of the treated sample for the final chromatography/detection step. The following aspects will be discussed specifically:

(1) cleaning of labware and reagents
(2) sampling
(3) transport and storage
(4) enrichment (cleanup)

(5) group separation (preseparation).

Derivatisation reactions, though often a very important part of sample treatment will not be considered. Excellent monographs exist on this topic [17,18].

A broad variety of matrices and types of molecules is encountered in organic trace analysis. Gaseous matrices such as clean air or head-space mixtures, gas/solid matrices as motor and chimney exhausts, liquid/solid matrices as sludges or lake muds, solid materials such as soil or fly ashes, biological materials as plants, blood, liver or adipose tissue represent by no means a complete list of matrices. This variety can be summarized according to the physical consistency of the matrices or often more important to the possible way of sample treatment. A basic rule in sample treatment should be to employ as general a scheme of separation techniques as possible, even though, specific steps may be necessary to handle specific matrices.

The complexity of the matrices is enhanced by the broad spectrum of analytical properties such as volatility, solubility, adsorptivity and partition characteristics of the molecules to be analyzed. For the sample treatment this means that despite all general approaches a broad spectrum of analytical techniques may be necessary. Therefore only the major rules of handling will be discussed for the matrices air [2,4,5,6,19], water [2,8,12], sediments [20], fly ash [21,22], plant material [11,15], blood [16,23], liver and adipose tissue [24,25] restricting myself to some matrices which our research group has gained some experience. The same limitation holds for the selection of the groups of chemicals which will be considered: Volatile organohalogens (Freons to hexachlorobenzene) chlorinated pesticides including the multicomponent mixtures Toxaphene, aliphatic and aromatic hydrocarbons, polychlorinated aromatics and oxyarenes (dibenzofurans and dibenzodioxins). The discussion of sample treatment will be oriented to the most widely used separation/detection techniques such as HPLC/UV, GC/FID, GC/ECD or GC/MSD.

CLEANING OF GLASSWARE AND INSTRUMENTS

Cleaning of glassware and instruments

Appropriate materials to be used in organic trace analysis are glass and stainless steel. If polymers are needed, plasticiser free polyethylene and teflon should be used. Due to its basic properties, polyvinylchloride (PVC) may contain up to 20 % plasticiser mostly phthalates and/or chlorinated compounds. Cleaning the glassware or metal containers with organic solvents (hexane, acetone, toluene) requires high purity solvents and rather large volumes of these expensive materials. A cheap and convenient method is heating the labware up to 400° Celsius in a stream of nitrogen purified by charcoal. After being cooled down, coarse contamination can be avoided by covering with clean alumina foil or keeping the material under clean bench conditions. Such extreme precautions are necessary when the baseline content of ubiquitious compounds (phthalates, polychlorobiphenyls, certain polyaromatic hydrocarbons) have to be analyzed. Absorbents can also be cleaned effectively by "baking out".

Purification of solvents

Though quite a broad spectrum of high purity solvents is commercially available the need for purification of a specific solvent can arise. The basic step of solvent purification is distillation employing an effective column (rectification). Distillation can also include cryogenic distillation. Purification by adsorbents mostly gives negative results, as solvents will clean the adsorbents instead.

The purification can be enhanced by combining distillation with a chemical reaction. In the case of aliphatic hydrocarbons it is common to add sodium metal or $LiAlH_4$ in order to reduce the level of organochlorines. One has to be aware of the fact, that only solvents with a boiling point above the melting point of sodium (m.p.: 97.8° C) can be cleaned effectively this way. Only the clean surface of the sodium metal droplets reacts with traces of e. g. CCl_4.

In the case of acetone addition of water to the solvent extraction with hexane or toluene, followed by freezing out of the water at -100° C is a somewhat elaborate but effective way of purification [20].

Photolytic degradation can also be used as a way of destruction of unwanted compounds. The basic requirement is an absorption of light by the compounds, that shall be destroyed. The normal mercury lamp will photolyse e.g. the polychlorobiphenyls very effectively [15,26]. Most aliphatic organochlorine compounds start to absorb at 250 nm with a 100 % absorption at 220 nm. Tetrachloroethene, a most common contaminant in organic solvents starts to absorb at about 380 nm with a strong increase below 300 nm. Thus a mercury lamp (254 nm main emission) can photolyse this compound effectively.

Cleaning of instruments

Besides the "baking out" technique, rinsing with purified solvents is the standard procedure for cleaning the instruments. It is advisable to use the glassware and even more important the syringes only for defined purposes or a defined concentration range. HPLC/UV, GC/FID and GC/MSD require concentrations in about the same range, whereas GC/ECD is often a factor of 1000 more sensitive. If a change is made from a high boiling solvent (e.g. toluene) to a low boiling (e.g. pentane) in a given flask or syringe, the rinse will have to be very extensive, since even after several rinsing steps (> 10) a signal of the higher boiling solvent can be detected in GC/MS.

Reference compounds and standard solutions

Though reference compounds and standard solutions are primarily part of the determination step, their appropriate handling is part of the controlling of blank values or laboratory contaminations. As far as possible storage and weighing in of reference compounds should be performed well separated from the analytical handling. All labware used for the preparation of standard solutions should be considered as highly contaminated and handled accordingly.

SAMPLING AND ENRICHMENT

Sampling and enrichment of gaseous matrices

The sampling of gaseous matrices can be done principally by:

(1) direct sampling in syringes (0.5 - 500 ml)
(2) direct sampling by compressing in suitable metal lined plastic bags, glass (max. 3 Bar) or metal containers (max. 10 Bar)
(3) cryogenic sampling (-78° C/solid CO_2; -180° C/liquid air)
(4) adsorption on organic or inorganic adsorbents
(5) absorption in organic solvents with or without cooling
(6) absorption under derivatisation.

All sampling methods except the cryogenic sampling can be used for storage purposes, though the chance of a loss or more likely of a contamination has to be considered.

Syringes and pressurized containers allow the sampling of millilitres to a few litres. The cryogenic method allows the sampling of up to some cubicmeters of air combined with a reduction of the basic matrix components such as nitrogen, oxygen and the noble gases. A 500 ml condensation trap filled with Raschig rings and cooled with liquid air allows flow rates of 300 - 400 litres/hour with no break-through of even the fluorochlorocarbons. If the cold trap has a volume of only 50 ml, it can be used as the sample loop of a gas sampling valve. The focussing of the substances prior to the analysis by high resolution gas chromatography is in this case done by a simple liquid nitrogen (LN_2) trapping in a fused silica capillary.

The most widely used method for high volume sampling is the adsorption of organic traces on inorganic adsorbents like SiO_2 gel or Mg-silicate (Florisil) or on organic adsorbents like charcoal, poly-2,6-diphenyl-phenoxyether (Tenax) or polyurethan-foam. The desorption is either done by solvents (CS_2; acetone; benzene) or by gas flow at higher temperatures (200 - 300° C). Since a solvent volume of less than 30 microlitres is never achieved, the solvent desorption technique has the advantage of allowing multiple analysis. This advantage of multiple analysis is coupled with the reduction of the initially collected volume by a factor of at least ten, more often by a factor of 100. This drawback of analyzing only part of the collected volume is not encountered when the high temperature desorption is coupled with a cold trap focussing. The thermal desorption can be achieved by heating in an oven [2, 19], resistance heating [2] or microwave heating [27]. If the weight of the adsorbent is small and the temperature rises fast, a secondary focussing may be omitted. Cryogenic sampling in combination with intermediate adsorption on Tenax and final liquid nitrogen trapping is a three step sampling/injection technique, which allows the analysis of up to 2 - 5 cubic meter of air as a single probe.

Sampling by absorption either based on solubility or followed by a derivatisation reaction in the absorption solution can be a very convenient method

of combining sampling and enrichment. The sampling by solubility-absorption is limited by the vapor pressure of the compounds of interest; Henry's law has to be remembered. Such an absorption-sampling can also be looked upon like the well known purging technique, which actually is a method of depletion. Absorption sampling can be extended by using low melting solvents such as methylcyclohexane (m.p.: -126° C) or isopropanol (m.p.: -89.5° C). Cooling with solid carbon dioxide (-78.5° C) or a sand bath cooled down to the temperature needed (-100° C) by liquid air is easily achieved.

Absorption followed by a reaction can be a very effective method of sampling smallest traces in high sample volumes. The simplest way is using the formation of a non-volatile salt (pentachlorophenol → sodium pentachlorophenolate) or a condensation reaction (formaldehyde → pentafluorophenylhydrazone). In the latter case sampling at an elevated temperature (50 - 70° C) can enhance the sampling effiniency due to an increased reaction rate.

Sampling and enrichment of particulates in gases

In practice often the question of sampling solid as well as gaseous emissions of e.g. chimney effluents is encountered. A differentiation of the phases can be of interest with respect to what part of the emission - particle or gas phase - unwanted compounds such as polyaromatic hydrocarbons or even polychlorodibenzodioxins and dibenzofurans are associated with.

The standard procedure consists of filtering off the solid particles on glass filters of defined pore sizes, followed by condensation of the water of the stack gas and then running three or more absorption devices as the final part of the so called sampling train [6]. A somewhat more elaborate way of sampling particles is the use of a cascade impactor, or less sophisticated using a midget impinger (flow rate commonly set at 3 litres/min) or a Greenberg-Smith impinger (flow rates up to 30 litres/min). While the midget impinger is used wet, the Greenberg-Smith impinger can be used wet or dry. The conditions of isokinetic sampling have to be obeyed [2,6].

High volume sampling for suspended particulates is done by using glass fibre filters and flow rates of 0.8 - 1.7 cubicmeter/min. The standard set up is used to collecting aerosol particles of less than 100 micrometer in diameter. The sampling time is normally 24 hours, equivalent to an air sample of 1440 cubicmeters when sampled at an average flow rate of 1 cubicmeter/min. [6].

Sampling and enrichment of organic trace from water

Sampling of organic traces from water is done either by

(1) purging with N_2 or He
(2) solvent partition
(3) adsorption techniques
(4) using bioaccumulation in fish.

The purging technique can be applied for compounds of high volatility and leads to the sampling techniques of gaseous matrices. Whereas solvent parti-

tion techniques are basically limited by the solubility of the extracting solvent in water and the partition coefficient of the compound, a more practical limitation is the time needed for mixing and separation of the two phases. A standard combination is the shaking or stirring of 2 l water and 10 ml hexane for up to 12 hours. The solubility of hexane in water is 50 mg/l. In many cases the solvent extract can be used for HPLC or GC directly. Extract of waste water or polluted river water require further preseparation steps.

The adsorption of organic traces on charcoal or on an organic polymer (XAD2; Tenax) or on a C_{18}-covered or otherwise modified silica is more or less independent of the amount of water put through. A practical limitation may arise from plain clogging of the adsorption tubes by algae or sediment particles.

If the pump, which is needed to force the water through the adsorption tube, is placed after the tube any contamination by the experimental set up is avoided. As mentioned before, the tubing prior to the adsorption tube should be made of glass or stainless steel. If organic materials are used, the loss of compounds or the contamination by the tubing has to be checked for.

The storage of water samples is best done by spin-freezing the water and then keeping it frozen. For this technique even glass bottles can be used.

For screening the pollution pattern of a river, a lake or even the sea the "sampling" by biological specimen, particularly by fish or birds, utilizing the bioaccumulation can be very helpful [28-30].

Sampling of soil, sediments and fly ash

Technically, the sampling of soil and sediments can be a simple procedure, but is complicated by the fact that it is often very difficult to collect a representative sample of the soil of interest. Different types of soil from the same area can give completely different results. The sampling of lake sediments can be hampered by muddy layers on top of the actual lake bottom. Those muddy layers as the most recent part of the sedimentation leading to geoaccumulation can be collected by a freezing technique [20,31]. Such samples as well as soils contain a varying amount of water and are often brought to air-dryness prior to the extraction step. The extraction can be done by the classical

(1) Soxhlet-method
(2) refluxing
(3) vapor phase extraction following a codestillation with water.

A mixed form of vapor phase extraction and solvent partition is obtained, when the solid matrix (soil, mud) but also tissue is refluxed in water/toluene (b.p. toluene 110.6° C) or water/alkane (b.p. n-heptane 98.4° C; b.p. i-octane 99.2° C).

The Soxhlet extraction uses continuously fresh solvent, thereby displacing any solubility equilibrium. The Soxhlet extraction of soil and air-dried

sediments was done by a mixture of hexane-acetone-methanol. The extracts were prepared for the analysis of aliphatic and aromatic hydrocarbons, polychlorobiphenyls and terphenyls as well as for chlorinated pesticides [20]. The refluxing technique combined with a final filtering or centrifugation of the undissolved solids employs higher temperatures, therefore favoring the desorption process. Extraction studies with fly ash proved the effectiveness of such a reflux-extraction as compared to Soxhlet extraction. A mixture of toluene/methoxyethanol (methylcellusolve) was used to which some concentrated hydrochloric acid had been added to improve the digestion of the fly ash [22].

Sampling of plant materials

Plant materials such as grass, hay, macroalgae or leaves require an extensive destruction of the macrostructure by grinding with sea-sand in a mortar or even better by a high speed blender. The extraction solvent has to contain some ethanol or isopropanol to penetrate the cellulose of the cell walls. The extraction of the homogenized sample is done as mentioned before by a Soxhlet or refluxing technique.

Sampling of blood, liver and adipose tissue

Sampling of blood is complicated by the fact that one can analyze either (1) whole blood, (2) serum, that is the liquid left after natural or induced coagulation, or (3) plasma, the liquid gained after the inhibition of the coagulation by heparin and centrifugation off of the red blood cells. In terms of analyzing for natural, pharmaceutical or xenobiotical constituents the whole blood or the plasma seems to be closest to a defined system.

Blood as well as plasma can be transformed into a solid matrix by adding enough anhydrous sodium sulfate and quartz sand to form a dry powder. This powder can be extracted either in a Soxhlet or as a column technique. Solvent partition techniques are often hampered by the formation of emulsions. This can be avoided by a type of homogenous extraction, where ethanol and isooctane are added to whole blood or plasma under ultrasonication prior to addition of 2 M $HClO_4$. The whole mixture is again ultrasonicated for five minutes and after addition of water is heated to 65 - 75° C for 10 minutes. Now the isooctane separates as a well defined phase [23]. Liver and adipose tissue are homogenized by grinding the sample with anhydrous sodium sulfate and quartz sand, adding enough to form a free flowing dry powder. This powder is treated as mentioned above for soil or plant material. A simple extraction technique is the so called column-extraction, where the sample is packed into a column and rinsed with the appropriate solvent.

The raw extract has to be cleaned from lipids and lipid-like material. This so called cleanup step is mostly done either by solvent/solvent partition or adsorption chromatography. The pairs hexane/acetonitrile or hexane/dimethylformamide are common combinations. Small amounts of lipids (50 - 500 mg) can be separated by adsorption chromatography on either magensium silicate (Florisil), alumimium oxide or silica. The water content of these adsorbents has to be controlled. Adsorption chromatography as the lipid cleanup can be

combined with a group separation of environmental compounds. The first eluate, mostly hexane or low boiling petroleum ether contains the aliphatic hydrocarbons, the chlorobenzenes, the polychlorobiphenyls (PCB) and the 4.4'-DDE. The second eluate, mostly combinations of hexane/diethyl ether, hexane/dichloromethane or hexane/toluene, contains the aromatic hydrocarbons (PAH), the chlorocyclohexanes, the polychlorocamphenes (Toxaphene), other compounds of the DDT group, the polychloroterphenyls and depending on the elution strength the epoxidic pesticides or metabolites [20,28]. The compounds of technical Chlordan are found in both eluates.

Enrichment of trace pollutants from marine oils

Oils from marine animals, such as cod liver oil, shark liver oil, menhaden oil or whale oil, of defined geographic origin are very suitable samples for analyzing the marine pollution. Due to the bioaccumulation and biomagnification of nonpolar persistent xenobiotics in fish enrichment factors of 10^5 are found [30]. The cleanup can be done as described before by solvent/solvent partition or adsorption chromatography. The efficiency of both cleanup procedures is documented in Table 1 and Table 2. If large amounts of lipid material (5 - 20 grams) have to be analyzed, the technique of cold precipitation can be very useful. The sample, typically 10 gram is dissolved in 100 ml acetone and 50 ml methanol are added at room temperature. The mixture is then cooled down in a sand bath to -100° C. After 20 to 30 minutes the bulk of the material has precipitated. The solvent is decanted and the precipitate is rinsed twice with a -100° C cold acetone/methanol mixture (1:1). Addition of 100 ml H_2O to the 170 ml solvent mixture separates the non-precipitated lipids, typically 5 - 10 % of the original amount, Table 3. This portion contains about all of the nonpolar xenobiotics. It is taken up in 10 ml hexane. The hexane solution can be used directly for the adsorption cleanup/group separation step. Though Florisil is still widely used for this purpose, silica (e.g. Merck Darmstadt) with an adjusted water content of 3 - 10 % after baking out at 500° C can be used instead. The group separation on silica has the advantage of a much better reproducibility.

Exclusion chromatography using Bio Beads SX-2 can also be used for lipid-matrix separation. As the Bio Beads are based on polystyrene, losses by adsorption effects are easily encountered and have to be checked for.

TRACE ANALYSIS OF SPECIFIC CHEMICAL GROUPS

Only a few chemical groups will be considered for the discussion of specific sample treatment techniques. These include:

(1) medium volatile aliphatic hydrocarbons C_8 - C_{34}
    (Fossil oils, natural background)
(2) aromatic hydrocarbons (PAH)
(3) volatile halocarbons (Freons, CCl_4, HCB)
(4) polychlorinated biphenyls (PCB)
(5) cyclodiene pesticides (Chlordan, Dieldrin)
(6) diphenylethane pesticides (DDT-group)
(7) polychlorocamphenes (Toxaphene)

Table 1:

Efficiency of DMF/hexane cleanup for marine samples.

Starting amount of lipids			Carry over of lipids
Cod liver oil		10 000 mg	563 mg
Extract of 20 g fish eggs			
Sturgeon (Casp. Sea)	1.	3 470 mg	223 mg
	2.	3 419 mg	183 mg
	3.	3 404 mg	272 mg
Salmon (Pacific)	4.	3 188 mg	488 mg
Oil fish liver extract		5 075 mg	2 301 mg
cleanup repeated		2 301	971 mg

Table 2:

Efficiency of combined DMF/hexane and Florisil (1.3 % H_2O) cleanup.

Step (1) DMF/hexane - partition:
10 g cod liver oil dissolved in 30 ml n-hexane. Extracted three times with 15 ml dimethylformamide. Reetraction into 3 x 20 ml n-hexane after addtition of 150 ml water.
Carry over of lipids: 563 mg = 5.63 %.

Step (2) Florisil - adsorption chromatography:
12 g Florisil (1.3 %) wet packed in n-hexane, 563 mg lipids.
Eluate 1: 40 ml n-hexane. Lipid residue: < 1 mg
Eluate 2: 40 ml n-hexane/5 % diethyl ether. Lipid residue: 66.8 mg
Eluate 3: 40 ml n-hexane/30 % diethyl ether. Lipid residue: 321 mg
Repeated chromatography of eluates 2 and 3 on 6 g Florisil (1.3 % H_2O) each:
Eluate 2.1: 40 ml n-hexane/5 % diethyl ether. Lipid residue: < 1 mg
Eluate 3.1: 40 ml n-hexane/30 % diethyl ether. Lipid residue: 296 mg

Table 3:

Efficiency of cleanup by cold precipitation of marine oils

Starting amount of oil		Carry over of lipids
Cod liver oil	10 g	1 860 mg
	3,0 g	180 mg
Menhaden fish oil	10 g	1 960 mg
	3,4 g	540 mg
Peru fish oil	10 g	1 300 mg
Sperm oil	10 g	490 mg
	3 g	130 mg

(8) polychlorooxyarene (PCDF, PCDD).

These groups of compounds form in themselves complex and often not fully identified mixtures. However each group contains compounds of similar properties in terms of volatility, solubility, adsorptivity and partition characteristics. Thus they require similar sampling and sample treatment techniques. Only selected techniques will be discussed as typical or inspiring examples, as a complete coverage cannot be achieved.

Medium volatile aliphatic hydrocarbons C_8 - C_{34}

The analysis of aliphatic C_8 - C_{34} hydrocarbons has its major applications in geochemistry and pollution analysis. The final separation/detection step will be high resolution gas chromatography with the flame ionisation detector. For that purpose a separation from aromatic hydrocarbons is the aim of any pretreatment scheme. Aliphatic and aromatic hydrocarbons can be separated by adsorption chromatography on e.g. Florisil (1.5 % H_2O) using pentane or hexane as eluent [20]. Separation from long chain waxes is not achieved this way, but can be done by pretreatment with concentrated sulfuric acid. In sediment samples elemental sulfur will elute with the aliphatic hydrocarbons. Though its FID signal is very small, the sulfur can be effectively eliminated by an activated silver reaction column [20] among other techniques. The silver reaction column also eliminates aliphatic sulfur-hydrocarbon compounds.

Aromatic hydrocarbons (PAH)

There exists an extensive literature dealing with the analysis of polyaromatic hydrocarbons [9]. The extraction should always include benzene or toluene as part of the solvent, since high molecular weight PAH show strong adsorption. Biological material should be saponified by alcoholic potassium hydroxide and PAH are then extracted into cyclohexane or methanol [32]. Solvent partition between alkane/nitromethane or alkane/dimethylformamide can be used for cleanup or separation purposes [9].
The same separation is achieved by adsorption chromatography with activated SiO_2 gel using isooctane for the first eluens and benzene as the second [33, 34].

Volatile halocarbons

For volatile halocarbons sampling and enrichment are highly connected. Due to their volatility any separation from liquid or solid matrices should go through the gaseous phase. The purging of water or of solids (soil, sludge, tissue) blended in water combined with either adsorption or cold trapping is an effective way of enrichment from non-gaseous samples [2].

Polychlorobiphenyls (PCB)

The polychlorobiphenyls appear to be the most widely spread group of pollutants found just about everywhere - including solvents and chemicals. The analytical chemistry of this group of 209 compounds is primarily a problem of contamination control. Their analytical behavior resembles in part that of the aliphatic hydrocarbons, e.g. the elution with hexane from SiO_2 gel or

Florisil, in part that of the aromatic hydrocarbons, e.g. the solvent partition hexane/dimethylformamide. The polychloroterphenyls are closer to the polyaromatics. The stability of PCB towards alkaline hydrolysis allows methanolic KOH digestions without affecting the amount of PCB. Short reaction times with concentrated sulfuric acid in the cold do not alter the PCB either. The PCB are however easily destroyed in the nanogram/millilitre ranges by UV radiation [26]. This can be used to identify them among aliphatic organohalogens or decrease blank levels in solvents.

The PCB are sampled from air by adsorption on Florisil or Tenax, and desorption either by acetone or thermally. Desorption by acetone allows a second step for enrichment: 0.1 - 0.3 millilitre of methylcyclohexane or toluene is added to the acetone, followed by adding 150 ml water. This homogeneous extraction allows the enrichment of PCB without changing the flask. Concentration by evaporation should be done by adding 20 - 30 microliter of a high boiling solvent (decane, xylene). In this way no losses are encountered.

The standard cleanup includes hexane/dimethylformamide partition followed by adsorption chromatography on either Florisil [28] or SiO_2 gel [35] with hexane or isooctane as eluents. Elemental sulfur is also found in this fraction, and can be removed by an activated silver column [20]. In extreme trace analysis of PCB the biologically modified pattern can be used as a check for contamination during the working-up procedure [30].

Chlorinated cyclodiene pesticides

Cyclodiene pesticides are found in environmental samples where either agricultural or health programs have included their application. The still widely used compounds of this group are dieldrin, α and β endosulfan and the compounds of the technical Chlordan. In the final step of group separation they appear in both the hexane and the hexane/diethyl ether or hexane/CH_2Cl_2 eluate.

Diphenylethane pesticides (DDT group)

Like the PCB the DDT group with the major compounds DDT, DDE and DDD, all three occuring as a mixture of the 4,4' and the 2,4' isomers, always is found in environmental samples. Its analytical behavior is close to that of the aromatic hydrocarbons with the exception of 4,4' DDE, which elutes e.g. with the hexane fraction from Florisil or SiO_2 gel. If the more polar metabolites such as the 2,2-di(4-chlorophenyl)acetic acid is looked for, the extraction and cleanup scheme have to be oriented to them. Alkaline hydrolysis of tissue leads to the formation of DDE from DDT, with the result that only the sum of DDT, Σ DDT, is accounted for.

Polychlorocamphenes (Toxaphene, Strobane)

The polychlorocamphenes are made by chlorination of turpentine oil and the production for 1980 in the United States alone amounted to 105 000 tons [36]. This complex mixtures of environmental pollutants has long escaped the analytical chemists. More than 670 compounds have been detected in the technical mixture of polychlorocamphenes [37]. Only by a clear cut preseparation

scheme combined with high resolution gas chromatography could its worldwide occurence be detected [28,35].
The environmental pattern of the polychlorocamphenes varies drastically since some of the constituents are partly biodegradable. During the standard clean-up by hexane/DMF partition and adsorption chromatography on either Florisil or SiO_2 gel the polychlorocamphenes are eluted in the hexane/diethyl ether eluate [28]. Only a few compounds will be found in the hexane eluate and can be mistaken for PCB components [30].

Polychlorooxyarenes (PCDF, PCDD)

The polychlorodibenzofurans (135 compounds) and polychlorodibenzodioxins (75 compounds) have gained world wide interest. Except for direct environmental contamination due to accidents or misplacing of chemical wastes, the major source of general importance for PCDF and PCDD is their occurence in fly ash from municipal incinerators.
The analytical properties of the PCDF/PCDD are governed by strong adsorption and low volatility. The strong adsorption has to be taken into account when extraction schemes are designed. In the case of fly ash one has to take care, that the extracting solvent definitely penetrates the particles. The effectiveness of the extraction by refluxing the fly ash with a mixture of toluene methoxyethanol (methylcellusolve) and concentrated HCl for 18 hours has been proved [22]. Extraction procedure applying only CH_2Cl_2 or benzene, whether with the help of ultrasonication or of the Soxhlet type are inadequate. The PCDF/PCDD are eluted from Florisil (1.5 % H_2O) by a mixture of toluene-diethyl ether (80 + 20). The PCDF/PCDD can be preseparated by reversed phase chromatography in a more defined way [21]. Such a specific preseparation can be of essential help in the identification step.

CONCLUSIONS

Though a broad variety of matrices has to be treated for an even broader spectrum of organic compounds, only a few basic elements of sample treatment exist. Enrichment and separation can be achieved by changing the phase, e.g. purging, partition or extraction, as well as removing by adsorption from the gaseous or liquid phase on to a solid. However the specific requirements of a given analytical problem may lead to a broad range of sample treatment techniques. But one should always be aware that there is rarely only one solution to a problem and the one, that is used, may by no means be the optimum.

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