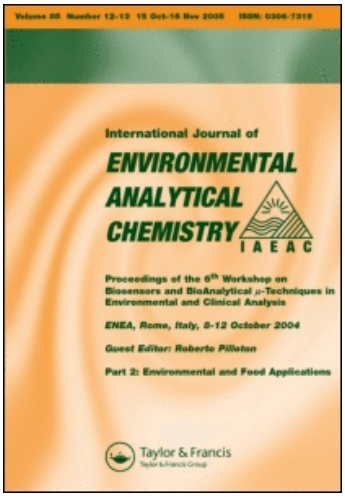

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Quantitative Analysis of Persistent Organochlorines in Samples From Polar Regions a Challenge For The Analytical Chemist

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QUANTITATIVE ANALYSIS OF PERSISTENT ORGANOCHLORINES IN SAMPLES FROM POLAR REGIONS A CHALLENGE FOR THE ANALYTICAL CHEMIST

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The study of the transport and fate of persistent polychlorinated compounds to remote areas such as polar regions requires analytical methods which are capable to detect fg to pg amounts in the main transport medium, the atmosphere, as well as their accumulation in the very short food chain. A list of requirements are given which have to be fulfilled for the detection of such compounds with sufficient reliability. Furthermore, problems observed during sample clean-up, separation and quantification of such low levels are discussed using practical examples, and proposals are made how to avoid them.

KEY WORDS: Chlorinated compounds, air, water, remote areas, sampling.

INTRODUCTION

During the past 20 years an increasing number of toxic persistent organochlorines have been detected in remote areas such as the polar regions. To start with, the available analytical methods did only allow to find chlorinated pesticides which are highly bioaccumulated in organisms such as p,p-DDT and hexachlorocyclohexanes. Furthermore, the lack of sensitivity and selectivity complicated the safe identification of such compounds in regions far away from source areas. Especially proofing that such substances can be transported over long distances via the atmosphere or by sea currents requires sampling techniques for large volumes of air or water as well as analytical methods for the determination of ppq- to ppt-concentrations. A survey is given about the measuring techniques which have been developed for ultratraces of persistent organochlorines in air, precipitation and biological material. The applicability of these methods will be demonstrated by selected examples.

Furthermore, some practical aspects will be discussed concerning the forever on-going struggle with contamination, compound losses by adsorption and interferences by the sample matrix.

SAMPLING MATERIAL AND SAMPLING METHODS

The levels of numerous toxic organochlorines are too low in the main transport media to polar regions such as air (precipitation) or water. However, many are able to bioaccumulate in organism by several orders of magnitude compared with the surrounding medium. This opens the possibility to detect their presence in remote areas by analysing organisms on top of the food chain.[1].

The only possibility to detect the very low levels of polychlorinated organics in air and water is to increase the sample volume. High volume air sampling using polyurethane (PUR) foam for adsorption of compounds in the vapour phase and collection of the particle-adsorbed fraction on a glass fibre filter allows to sample volumes of more than 1000–5000 m^3 of air[2]. The amounts being present in surface water can be concentrated on polymeric solid adsorbents by passing volumes of 1000 l or more through PUR-foams or divinylbenzene/styrene copolymers (e.g. XAD-2). However, colloidal dissolved organochlorines are not completely retained on such surfaces, and substantial losses might occur compared with classical solvent extraction methods[3].

In most cases sample extraction is still carried out in the classical way by either soxhlet or fat extraction (biological material). Supercritical fluid extraction is often not practicable for such type of ultra trace analysis due to the limited sample amount which can be extracted, the insufficient purity of the supercritical CO_2 and/or the not complete extraction of pg-amounts due to adsorption effects.

CHOICE OF ANALYTICAL TECHNIQUES

Sample clean-up

In samples from remote areas compound amounts in the range of fg to pg have to be quantified in a complex sample matrix. This requires extensive clean-up procedures. Furthermore, the risk for contamination by carryover between samples, impurities in solvents or losses by adsorption effects has to be minimised. For classical column chromatography, only carefully cleaned adsorbents such as silica and aluminium oxide should be used, preferably in disposable columns (e.g. Pasteur pipettes). Furthermore, the amount of adsorbents used should be kept at a minimum (ca. 1–3 g) to avoid losses by irreversible adsorption.

To compensate for the reduced sample capacity of such small columns, it is advisable to remove the major part of the sample matrix in advance by e.g. gel permeation chromatography. This technique allows also to isolate selectively a fraction with the molecular range of interest, and the risk for sample carryover is very small. It can also be easily automated.

Such precleaned sample extracts can be fractionated further according to compound polarity. Silica coated with 40% sulphuric acid (removes all non-persistent compounds) or potassium hydroxide (saponification and removal of fat) are also very useful adsorbents for the clean-up by liquid chromatography. However, the analysis of very complex substance classes in the sample such as polychlorinated biphenyls (PCB), dibenzofurans (PCDF), dibenzo-p-dioxins (PCDD) and camphenes (Toxaphene) requires more sophisticated clean-up techniques[4]. Special columns based on activated charcoal can be used to concentrate selectively planar polychlorinated aromatics such as PCDF, PCDD and non-ortho(coplanar) PCB (coPCB). High resolution liquid chromatography is an efficient methods to separate PCB from toxaphenes.

Ultra trace analysis of persistent organochlorines is very expensive. When a large number of samples has to be analysed, it is advisable to carry out a less costly screening analysis first. On the basis of these results samples can be selected for a more comprehensive analysis including a large number of compounds. However, it should always be tried to develop clean-up procedures which allow the simultaneous isolation of as many compounds as possible. Only in this way a cost-efficient ultra trace analysis can be carried out. Figure 1 shows an example of a clean-up scheme for persistent organochlorines in different samples matrixes.

Separation and quantification techniques

High resolution gas chromatography (HRGC) is in most cases the only separation technique which minimises interferences by co-eluting compounds and which gives the best possible isomer selectivity for the analysis of complex compound classes such as PCB, PCDF/PCDD and toxaphenes.

Another important aspect is the separation of enantiomers as shown recently[5]. Many persistent organochlorines such as α-HCH, cis/trans-chlordane and toxaphenes are present as racemates (1:1 enantiomer ratio) in the applied technical products. However, the biological activity of the enantiomers is normally quite different. In many cases only one is biological active. Normally, there are big differences between enantiomers concerning bioaccumulation, metabolisation and toxicity. Therefore, an enantiomer-selective separation of such compounds is of great importance. As shown recently, the 1:1 racemate ratio of α-HCH is significantly altered in the environment due biological degradations.

HRGC has to be combined with detection methods which allow a safe identification of substances at very low concentration levels. Classical GC-detectors such as the flame ionisation or electron capture detector (ECD) have an insufficient selectivity for the unequivocal confirmation of the presence of a compound. They are at best case suitable for a screening analysis of samples from polar regions. Quantification should be carried out by mass spectrometry. High resolution electron impact ionisation mass spectrometry (HRMS) at e.g. resolution 10'000 allows to quantify compound amounts in the low fg-range with very high selectivity. An alternative method is low resolution negative ion chemical ionisation (NICI) mass spectrometry. It has a very high selectivity for polychlorinated compounds with detection limits of 0.1–1 pg.

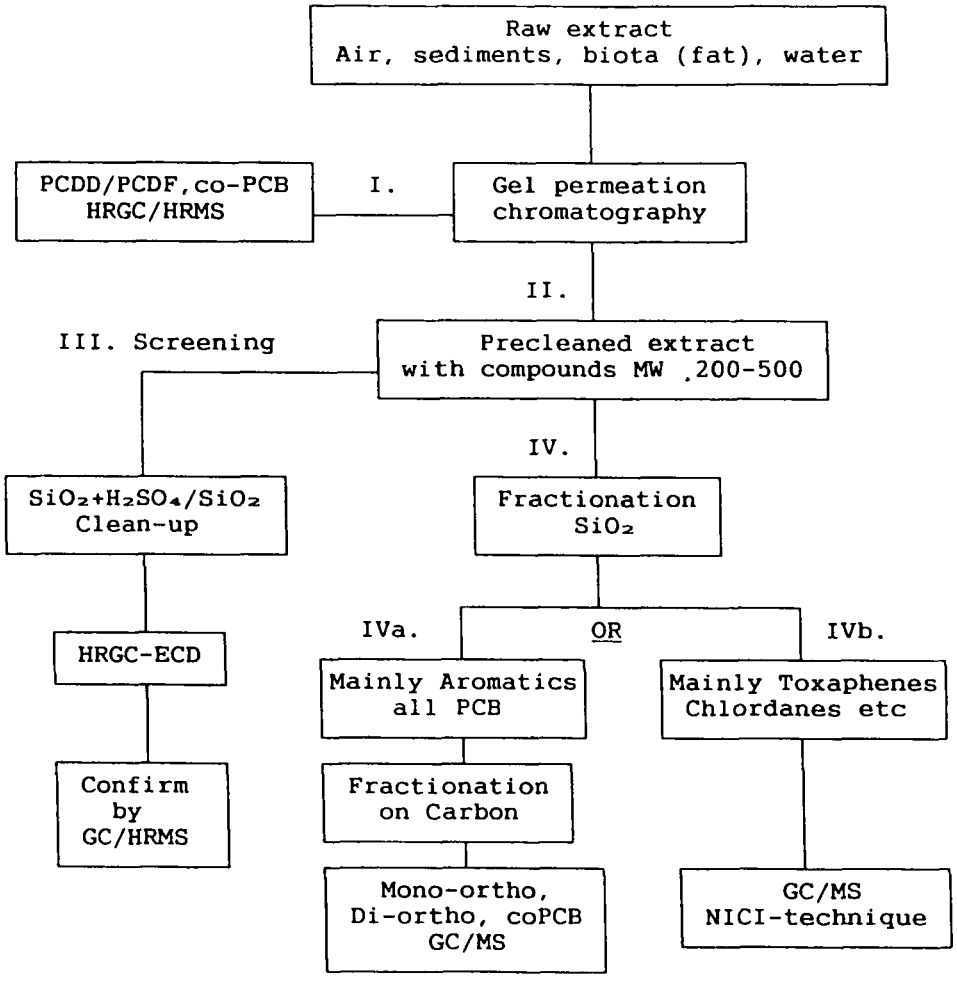

Figure 1: Analysis scheme for persistent organochlorines in different sample matrices from remote areas.

Quantification should preferably be carried out by the isotope dilution technique. Isotope-labelled compounds are added to the sample prior to clean-up and act as internal standards. However, this is not possible for screening techniques using an ECD. In this case compounds have to be added as internal standards which normally are not present in the samples such as 1,2,3,4-tetrachloro- and octachloronaphthalene or heptachlor (after H_2SO_4 pretreatment). In some cases even highly isotope-labelled compounds can be employed which are gaschromatographically separated from the natives due to the isotope effect. $^2H_6{}^{13}C_6$-gamma-hexachlorocyclohexane or completely deuterated polycyclic aromatics are examples.

However, the lack of pure and certified reference compounds limits still the quantitative analysis of some compound classes such as toxaphenes or chlorinated naphthalenes[6].

PRACTICAL PROBLEMS

Contamination

The biggest problem when analysing samples from remote areas is the everywhere present risk for contamination. Pesticide-grade solvents are now in most cases of sufficient quality. However, the screw caps of the solvent bottles might contain materials of doubtful quality such as sealings made from aluminium-coated cardboard which is able to contaminate the content after a certain period. Glassware can also be the origin of interfering compounds or cross contamination. In most cases careful rinsing with a detergent followed by distilled water and a clean solvent is not enough. Heating the surface to about 450–500°C (only borosilicate glass) in a glassblower furnace is an efficient measure to remove adsorbed trace amount of persistent organochlorines. In general the use of Teflon or other plastic materials (e.g. stoppers, tubing) should be avoided whenever possible.

Moreover, it can be necessary to split the activities in the laboratory into low and ultra low level work by marking carefully all equipment according to its use. Concentrating sample extracts to a few micro- or millilitres can also be the source of contamination by e.g. phthalates from vacuum tubes.

Solid adsorbents such as silica and aluminium oxide should not be purchased or stored in plastic bottles. Their purity has to be controlled carefully. Cleaning of such absorbents and inorganic salts such as sodium sulphate for drying can be easily performed by heating them to 300–450°C for several hours. However, after such a procedure the activity grade has to be adjusted. Glass wool (especially silanised qualities) can contain enormous amounts of impurities. In the best case soxhlet-extraction will help, in the worst case it cannot be used at all. However, normal cotton wool is a very good alternative. It can be easily cleaned by solvent extraction and does not show compound losses due to surface adsorption.

Contamination of cleaned sample extracts due to impurities from the septum cap of the sample vials is still a problem. Only pure (normally colourless) silicone septa coated with a Teflon-layer should be used. After perforation with a syringe needle, they have to be replaced immediately by a new one.

Compound losses

Losses of relatively low-boiling compounds such as chlorobenzenes or HCH during solvent evaporation might also be severe. Evaporation to dryness should always be avoided. Adding a small amount of a high-boiling solvent as a "keeper" and use of reduced vacuum combined with a gentle flow of purified N_2 directed to the solvent surface minimises evaporation losses.

Compound losses may also occur during sample clean-up. Especially larger amounts of aluminium oxide (>3 g) may cause irreversible adsorption. Furthermore, the activity of the adsorbents has to be controlled very carefully. Glass sinters should be avoided. They trap small adsorbent particles which may both cause adsorbent losses and sample contamination.

Thermal decomposition in GC splitless injectors can also be substantial when injecting low pg-amounts. A good test of the inertness of the glass liner is an injection of heptachlor which is easily converted to heptachlorepoxide on even slightly active surfaces. The use of glass wool should be avoided whenever possible. Direct on-column injection helps to overcome the problems mentioned above. However, due to the extremely high sample concentration factor, matrix residues are often present in the extracts which are then deposited in the capillary column. After a few injections irreversible losses of fg-pg amounts might occur on such layers.

CONCLUSIONS

Ultra trace analysis of persistent organochlorines is a very difficult task which needs a lot of experimental skill and experience. The main sources for contamination are solvents, glassware, solvent evaporation and cross contamination between samples. The recommendations mentioned above help to avoid them. References[1,2,7,8] give a survey about the results obtained so far with the methods described above.

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