ANALYSIS OF ORGANIC MICROPOLLUTANTS IN WATER

Proceedings of the Second European Symposium held in Killarney (Ireland), November 17-19, 1981

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FOREWORD

The Commission of the European Communities presents with this volume the proceedings and the conclusions of the second European Symposium on the analysis of organic micropollutants in water.

This symposium has been organized within the framework of the Concerted Action "Analysis of Organic Micropollutants in Water". This research programme is jointly implemented by the European Communities and Norway, Portugal, Spain, Sweden, Switzerland and Yugoslavia within the framework of a COST (Coopération Scientifique et Technique) agreement. The project, also known as COST Project 64b bis, aims at coordinating all relevant research in this field in the participating countries.

An effort is made to improve methods and techniques for the identification and quantitative determination of organic compounds present in all types of water.

The symposium permitted to review the results achieved during the past three years of research in the following areas:

- Sampling and sample treatment
- Gas-chromatography
- Separation of non-volatile compounds, in particular high performance liquid chromatography (HPLC)
- Mass-spectrometry
- Data processing
- Specific analytical problems, in particular the analysis of organic halogens and phenolic compounds.

The volume gives a rather complete overview of the activities in this field in Europe.

We are confident that it constitutes a valuable contribution to solving the important problems posed by the huge number of already identified or yet unknown organic pollutants in water.

The Commission of the European Communities wishes to express their sincere thanks to the co-organizers, the National Board for Science and Technology, Dublin and An Foras Forbartha, Dublin.

Brussels, December 1981

G. ANGELETTI H. OTT

Directorate-General for Science,
Research and Development,
Commission of the European Communities,
Brussels

C O N T E N T S

原书模糊

SESSION II - GAS-CHROMATOGRAPHY

SESSION III - SEPARATION AND ANALYSIS OF NON-VOLATILE COMPOUNDS

SESSION IV - MASS-SPECTROMETRY

SESSION V - DATA PROCESSING

SESSION VI - SPECIFIC ANALYTICAL PROBLEMS

A. Organic halogens

ANALYSIS OF ORGANIC MICROPOLLUTANTS IN WATER - - SOME INTRODUCTORY REMARKS

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The Commission of the European Communities has a number of projects aimed at Cooperation in Science and Technology, the socalled COST projects. One of these projects, the COST 64b-bis is directed towards the study of "Organic micropollutants in water". This is a subject which has attracted large interest both among the member countries, as well as many non-member countries. However, when we look at the different problems and research interests in the various countries, we realize that they span a very broad research area. There are different environmental problems in the southernmost compared to the northernmost countries in Europe, as well as the easternmost compared to the westernmost ones. We, in the scientific committee of the COST 64b-bis project, have tried to reflect this when composing the program. Over the three days to come we will have a good opportunity to look into several aspects of analysis of micropollutants in water.

If we take a few moments and look back into history, we will realize that water pollution is not a new problem. The laws established over three thousand years ago by Moses detail how human waste should be disposed of by burial outside the immediate confines of the camp and away from running water which may be used for drinking purposes. The large sewer in Rome, the "Cloaca maxima" build by the Emperor Tarquinius was not only constructed for esthetic reasons, but rather for the practical purposes of avoiding diseases and protecting ground water supplies. About year 1250 water pollution legislation was introduced in Venice and in 1501 laws were promulgated in Paris to protect the water of the Seine from the discharges of the growing City. And an unpleasant situation in year 1800 was very nicely described by Samuel Coleridge when he wrote the poem,

> The River Rhine, it is well known
> Doth wash your city of Cologne
> But tell me, nymphs, what power divine
> Shall henceforth wash the River Rhine.

Over the years there has been a great effort to clean most of the polluting discharges from municipal, agricultural and industrial sources, and much has been achieved in terms of removing major pollutants from our environment. In recent years there has also been a large interest for organic micropollutants in water. The reason for this interest is of course the possibilities for some of these micropollutants to bioaccumulate due to their chemical and biological persistence or to have long-term effect.

Furthermore, what is also characteristic for the development in the area of pollution studies are the very strong ties between environmental chemistry and analytical chemistry. In many respects we have seen that the development of analytical methods has revealed new environmental problems. This is true both for organic and inorganic pollutants. On the organic side, I only have to mention the importance of chromatographic

techniques, such as gas chromatography and high performance liquid chromatography. To some extent, it is also true that realization of environmental problems has created a demand for new analytical instrumentation. I believe that the development of for instance modern mass spectrometry has been very important for the development of environmental chemistry. On the other hand, the demand for better analytical methods has provided a great push for the development of mass spectrometric instrumentation. It is apparent that some of the manufacturers of mass spectrometric equipment would not have existed without the market created by the environmental protection legislation.

The relation between analytical chemistry and environmental chemistry has several dimensions. First of all we have been working continually to improve the analytical sensitivity. Our interest is frequently focused on compounds which occur in very low concentrations. Furthermore, we are interested in the specificity of the chemical compounds. We cannot use collective parameters only, but we also like to know exactly what kind of chemical species are present. These two analytical aspects, sensitivity and specificity, are then used in environmental interpretations. It is important to know what kind of pathways or fates the chemicals in the environment undergo, if there is any bioaccumulation or biodegradation, what are the environmental or health effects, is it chronic or acute toxicity, are the compounds mutagenic or carcinogenic and so on. The interrelation between these three parameters is illustrated in Figure 1.

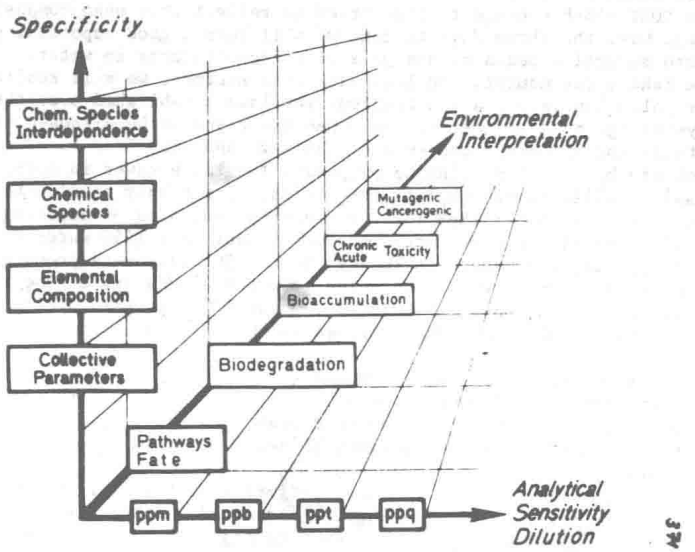

Figure 1. The interrelation between analytical Sensitivity, Specificity and Environmental Interpretation (W. Stumm and R. Schwarzenbach, EAWAG, 1980).

As seen the analytical sensitivity may vary over several orders of magnitude. We also have to consider the specificity of our determinations. We can determine the collective parameters, we can determine elemental compositions of the individual chemical species and we can determine the chemi-

cal species' interdependence. In our studies of organic micropollutants in water these three dimension aspects are very important.

Recently, we have also seen that studies of organic micropollutants in water put increased requirements on the analytical methods in terms of both qualitative and quantitative aspects. New and improved methods are needed for monitoring and inventory of pollutants as well as studies of transport and fate of organic pollutants in the aquatic environment.

The aim of this Symposium is to try to look into the state-of-the-art of certain areas related to organic micropollutants in water and to discuss their future trends. We, in the scientific committee for this meeting, have selected to discuss topics such as sampling, analytical methods, data handling and finally specific groups of pollutants. The concepts of sampling methodology will be subject for thorough discussion during this meeting. Concerning analytical methods we will discuss of course, the well known techniques capillary gas chromatography and high performance liquid chromatography. In addition we will look specifically into the combination of HPLC and mass spectrometry, and we will look to mass spectrometry as a technique by itself, the socalled MS-MS-techniques. Particularly interesting subject in this area is also the computerized data collection handling and interpretation. Organic pollutants in water comprise a large number of compounds, or groups of compounds. Among the groups that we have selected as particularly important in the current state, are the organic halogenated compounds and phenolic compounds, but other compounds will also be discussed. I believe that this program comprises a combination of focusing on technical problems as well as the application of highly advanced techniques.

SESSION I - SAMPLING AND SAMPLE TREATMENT

Chairman: F. BRINKMANN, National Institute for Water Supply, The Netherlands

Review paper :

- Recent concepts in sampling methodology

Short papers :

- A new method for the quantitative analysis of organochlorine pesticides and polychlorinated biphenyls
- Concentration and identification of the main organic micro-pollutants classes in waters

Poster papers :

- Recovery of organic micropollutants
- Influence of humus with time on organic pollutants and comparison of two analytical methods for analysing organic pollutants in humus water
- Improved accumulation of organophosphates from aqueous media by formation of ion-associates with tetraphenylarsonium cation
- The use of ECD and FID fingerprint techniques for the evaluation of river water purification contaminated with organic pollutants
- Lekkerkerk

RECENT CONCEPTS IN SAMPLING METHODOLOGY

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Summary

Sampling of different kind of waters is discussed. Since the sampling is an integral part of the whole analytical procedure, different method designs are treated with such aspects as sensitivity, selectivity and convenience. Various small-volume sampling methods are exemplified for predetermined compounds. Results from comparative studies of different standard methods are shortly reviewed. Continuous automatic sampling by solvent extraction and by preconcentration on sorbents, to obtain representative samples over a period of time, are compared. Particulate matter in the water may cause systematic error in the sampling stage.

1. INTRODUCTION

Water sampling is not simple. Sampling theory cannot replace experience and good judgement. The reliability of any analytical measurement is directly coupled to the uncertainties of the sampling process, or to sample storage, preservation, or pretreatment prior to analysis. The analytical process involves a chain of operations, where a significant error may be introduced at any stage. No chain is stronger than its weakest link, and this axiom applies also to the analysis of water for its composition. If the sampling is not correctly performed, the most refined techniques and sensitive instrumentation will not automatically lead to reliable and accurate results. The sampling is the first step and probably the most essential step in the analysis. The classical statistical theory of sampling cannot be applied to water, since its environment is influenced by chemical physical, and biological processes, resulting in a pronounced variability of the momentary distribution. The large variety of different processes which influence the distribution of the compounds in question requires a good knowledge of water chemistry.

In this paper the sampling strategy will primarily be discussed. Since in most cases the sampling is an integral part of the whole analytical procedure, the method design will also be treated.

1.1 Sampling strategy for different waters

Knowledge about the nature of the water to be sampled is important. The distribution and transportation of organic micropollutants in natural water systems are influenced by the interaction between the dissolved and the particulate components. When liquid-liquid extraction procedures are used for the preconcentration of organics, the partition coefficient determines the yield. The partition coefficient in turn varies with the concentration of suspended solids. The nature and characteristics of the adsorbing solids are significant factors, e.g. the greater capacity of

organic matter to adsorb in contrast to the sands. The volatilization of organics from water bodies is to a great extent dependent on oxygen content, temperature, hydrodynamics, etc. Thus, organic micropollutants may behave very different in river waters compared to sea water.

Sea water and ground water are very different in composition. Sea water contains besides inorganics a lot of particulate organic matter, e.g. organisms, cells, colloidals, and in addition dissolved organics. Ground water is protected from atmospheric influence and filtrated through e.g. sand, which means that the water is low in particulates and easily retains volatiles. Of course, these entirely different characteristics must be considered in the selection of sampling methods.

The dispersion pattern of organic substances in the sea is quite different from that in rivers. Meteorological circumstances may influence in such a way that sampling can only be carried out during controlled and stable conditions, which requires fast collection of samples.

The concentration of organics in urban run off water depends on the precipitation. Pollutants may have been accumulated during a long period of time with no rainfall. The first rainfall will then wash away high concentrations of particulate solids. The majority of the extractable organics, is carried by the solids.

Tap water is relatively convenient to collect, which often may be done already at the laboratory. The drinking water composition varies very little compared to other types of water. Therefore, sampling methods for drinking water may be easier to standardize.

Occasional discharges into recipients are very difficult to trace and especially quantitate. Grab sampling or integrated sampling techniques have to be considered according to convenience and the stated goal. The frequency of grab samples may be very high to balance integrated sampling performed in a continuous system. In many cases it is impossible to solve a pollution problem with grab sample collection. When monitoring a river system for occasional discharges, a continuous-collection strategy is a requirement for tracing suddenly appearing pollutants from unknown sources.

Continuous sampling may be performed in discrete steps, as with the spoon sampler. This water collector is not reliable for volatile compounds, e.g. oil constituents, which will partly evaporate during the sampling time. Continuous sampling involves very frequently a preconcentration step. Liquid-liquid extraction and adsorption on adsorbents are then the common techniques. The former technique leads to the extracted compounds being preserved in the organic phase. Grab sampling requires different preservation methods during storage. Ideally, full analysis should be conducted on the spot, immediately after the sample is taken.

The collection of sea water samples for oil analysis is connected with great contamination risks. The water surface around the ship is covered with a thin film of oil emanating from the ship. Furthermore, the atmosphere around the ship is polluted with diesel smoke, which necessitates an avoidance of atmospheric exposure of the sample. The sampler has to penetrate the oil film without being contaminated. This can be carried out with a closed sampling bottle, which opens at the desired depth. The bottle is then used for the solvent extraction; thereby manupulative steps, as pouring, are omitted, which otherwise cause exposure to the air. Closed sampling systems are always desirable in trace analysis.

2. SAMPLING AS AN INTEGRAL PART OF THE ANALYTICAL METHODS

An analytical method to determine trace organics in water often consists of a series of operations. It is desirable to use as few