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## POSSIBILITIES AND LIMITATIONS OF TRACING INDUSTRIAL EFFLUENTS IN THE SEA BY MEANS OF CAPILLARY CHROMATOGRAPHY

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### SUMMARY

Certain organic constituents of waste water, such as halocarbons and chlorophenols, can be used to establish the distribution pattern of effluents discharged into the sea. The approach requires simple sampling techniques and highly sensitive and rapid analytical methods. The combination of glass capillary column gas chromatography and electron-capture-detection meets the analytical requirements. The selectivity of the detector, together with the high resolving power of the column, makes it possible to handle the complex sea-water matrix. Selective derivatization directly in the water sample is combined with simultaneous extraction to increase the number of suitable tracers. Halocarbons can be measured at  $\mu\text{g/l}$  levels. Chlorophenols are determined at  $\text{ng/l}$  concentration levels.

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### INTRODUCTION

Ever-increasing demands are placed on natural waters for the disposal of man's waste products. To protect the aquatic environment, it is essential that the capacity of these waters for assimilating wastes be known. The dispersion of pollutants in water is mainly governed by dilution and by the reactivity of the discharged pollutants. Most dispersion studies have been carried out with fluorescent dyes, added as a tracer<sup>1</sup>. Fluorescence techniques are sensitive and practical for continuous monitoring, and *in situ* measurements of tracer concentrations can often provide adequate statistical information. A useful tracer should either mix conservatively or else decay in a simple, predictable manner. However, fluorescing dyes, such as Rhodamine, may undergo chemical alterations or become adsorbed on particles, and this will complicate the mapping. Radioactive isotopes, such as <sup>82</sup>Br, have constant decay rates and have the advantage that the tracer is not adsorbed on suspended particles. They are also relatively easy to detect *in situ*. However, there are risks and restrictions associated with the use of radioactive isotopes.

Certain organic constituents already present in waste water may be used for distribution studies<sup>2</sup>. One then has the advantage of a continuous supply of the tracer. Among these compounds, one may select those for analysis which are known to have environmental impact. If the prerequisite that the compounds can easily be

measured at very low concentration is met, it will be possible to establish a distribution pattern over a very large area surrounding the discharge site. With the aid of this information, the water-mass circulation pattern can be evaluated.

When designing methods for monitoring tracers in coastal waters, the following requirements should be met:

1. Extremely high sensitivity to match the high dilution in the recipient.
2. Simplicity in handling and pretreatment of the sample.
3. Instrumentation sufficiently simple and rugged that it can be used on board a ship.
4. Rapidity of measurement in order to process the large number of samples required to obtain a statistical basis for distribution models within a short period.
5. Possibility of using a wide range of different tracers with different properties.

Glass capillary column gas chromatography (GC) has been developed to the point where it has the efficiency to meet the requirements for separation and detection. However, the entire method must be optimized since the sampling, the sample pretreatment, the injection technique and the detection are dependent on each other. For the sake of simplicity, in the following the instrumental part is treated separately from the sampling and sample pretreatment.

## INSTRUMENTATION

### *Detector*

Ultimately it is the detector sensitivity which determines the capability of the method. In practice, only electron-capture detection (ECD) and mass spectrometry in the selective-ion detection mode fulfil the demands for sensitivity and selectivity. Since the mass spectrometer is not sufficient portable, it will not be discussed here.

The electron-capture detector has been used with great success for tracing halocarbons in the atmosphere<sup>3</sup>. The sensitivity of this detector is extremely high and in combination with glass capillary columns it has the potential of detecting femtogram amounts of compounds with high electron affinities, such as some halocarbons<sup>4</sup>. Since the electron-capture detector is a concentration-dependent detector, a very high sensitivity is obtained with capillary column separations, which yield narrow peaks. The low carrier gas flow-rate in capillary columns is incompatible with the dead-volume of the detector cell, but this can be overcome by adding a make-up gas (commonly 30 ml/min) at the end of the column. This preserves the separation efficiency. The somewhat lower detector sensitivity due to sample dilution is acceptable.

Selectivity is an important property of the detector. It refers to the ability of the detector to discriminate between the compound of interest and other extracted material. The selectivity of the ECD response is very broad in that the response to different compounds varies within six orders of magnitude<sup>5</sup>. Halogenated compound and nitroaromatics give a particularly high response. Many of these compounds are potentially hazardous environmental contaminants and thus ideal for tracing studies.

### *Injection techniques*

A principal requirement for trace analysis is sensitivity. This is very important when considering the amount of sample that must be injected to produce a reliable

peak. If the detector sensitivity is insufficient, more sample must be injected. Although injection volumes do not usually exceed a few microlitres, Fogelqvist and Larsson<sup>6</sup> have found that it is possible to inject large volumes (up to 250  $\mu\text{l}$ ) of pentane solutions for halocarbon determinations. This has improved the sensitivity by about one order of magnitude. Room-temperature on-column injection was used in combination with a wide-bore immobilized SE-54 column.

Direct injection of water samples would be very practical. However, water is not compatible with existing capillary columns<sup>4</sup>. To solve this problem, a dual-column system for selective sampling has been proposed<sup>7</sup>. However, these systems are not reliable, since non-volatile constituents, such as sea-salt, accumulate.

#### SAMPLE PRETREATMENT

Water samples should be collected in such a way that the tracer substances are not affected. The sampler should consist of chemically inert material. Poly(vinyl chloride) (PVC) is not reliable in any part of the sampling system, since it yields ECD-sensitive contaminants. Small volume samples are kept in brimful, stoppered glass bottles to control side reactions and evaporation losses. A sensitive detector permits the use of small sample volumes. Following sampling, the substances of interest must be fixed. This is done by adding a solvent or a reagent solution, or both, as fast as possible.

Some techniques which meet the requirement of simplicity include partitioning with an organic solvent (liquid-liquid extraction) and, for volatile compounds with a gaseous phase above the water, headspace methods. However, the latter have limited use, since the most volatile substances are not adequate tracers. Dynamic headspace techniques, which may be used for less volatile substances, are not convenient in monitoring programs involving a large numbers of samples<sup>8</sup>. Liquid-liquid extraction, the most practiced and general, of the pre-concentration techniques, is preferable, but the extracting solvent should be compatible with the succeeding GC-ECD analysis.

Pentane extraction of halocarbons from sea-water is a straightforward pre-concentration procedure and meets the requirements of simplicity and rapidly. The extremely high sensitivity (in the pg/l range), together with the selectivity of ECD, make it possible to trace halocarbons very far from the source<sup>9</sup>. Actually, some halocarbons are found everywhere and thus constitute a background<sup>10</sup>. The high sensitivity is in part due to the large injection volumes and to the resolving power of capillary columns. The method is limited by the purity of the pentane rather than by instrumental factors.

Halocarbons are connected with a number of industrial activities and especially with various chlorination procedures. As tracer substances, they are nearly ideal, although there is some loss to the atmosphere which should be taken into account. Some halocarbons are of biogenic origin, *e.g.*, bromoform<sup>11</sup>.

Although a detector may be capable of detecting subnanogram quantities of a compound, it may not necessarily be capable of detecting low concentrations in a sample where many other extractives are present. When the extraction can be combined with the simultaneous addition of a reagent/solution, the sample pretreatment is still acceptably simple and rapid. Chemical derivatization directly in the water

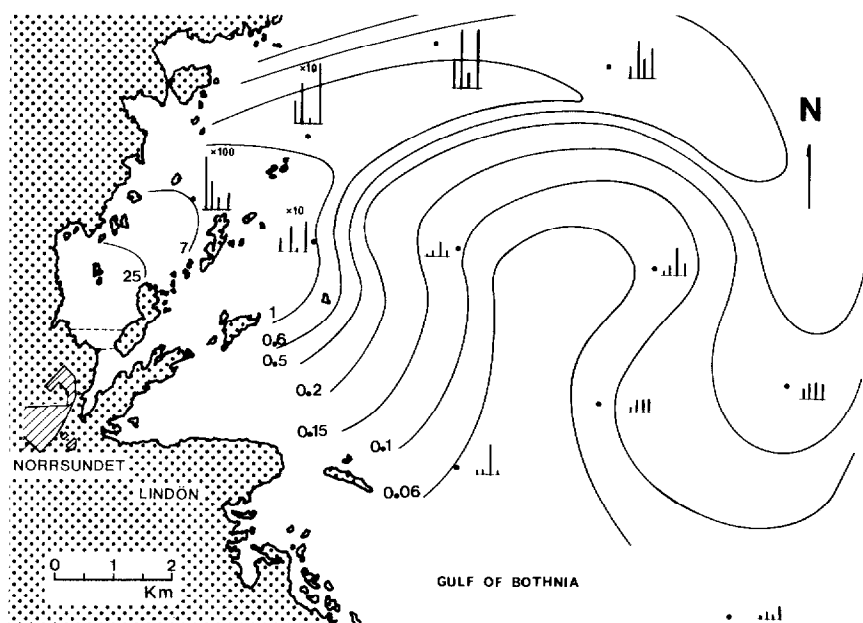


Fig. 1. Chloroform concentration isopleths ( $\mu\text{g/l}$ ) illustrating the distribution pattern of the effluent from a sulphate-pulp mill. Inserted are histograms, showing the concentrations levels of 2,4,6-trichlorophenol, 3,4,5-trichloroguaiacol, pentachlorophenol and tetrachloroguaiacol (left to right) at 2 m depth. The heights of the smallest bars correspond to 1 ng/l in 100-ml samples. These were the lowest concentrations measured.

sample is the method of choice for preparing the analytes for determination by chromatographic techniques. The derivatization can enhance the detector response by the attachment of groups that have a high affinity for electrons. Furthermore, the lipophilicity can be increased for the purpose of improving the extraction yield and chromatographic properties.

Extractive alkylation of carboxylic acids and phenols with pentafluorobenzyl bromide is a convenient method, since both extraction and derivatization are carried out in one step directly on a small-volume water sample<sup>12</sup>. The derivatives formed have a high electron affinity. The derivatization can be directed at certain classes of substances by pH adjustment. The drawback of the method is that excess of reagent and hydrolysis products interfere in the chromatogram.

Polar compounds, such as chlorophenols, are sensitive to ECD. By acetylating these compounds directly in buffered water samples, the products can be extracted quantitatively and separated by GC. Abrahamsson and Xie<sup>13</sup> have shown that the derivatization and extraction can be performed in one step and within 3 min. There is no problem with excess of reagent or hydrolysis products, and enrichment or clean-up are not necessary. The method can be used to determine chlorophenols in sea-water at the lower nanogram per litre concentration levels on 100-ml samples.

## RESULTS

The methods for halocarbon and chlorophenol determination have been used

to study the distribution pattern of pulp-mill effluents, discharged into the sea. The methods complement each other very well and can be used to determine spreading and dilution of ecologically hazardous substances and to trace water-mass movements. Fig. 1 shows an example of typical results of pollution from a sulphate-pulp mill.

The methods can be used to trace the effect of many other industrial activities, since the substances concerned occur frequently. The GC methods, optimized with regard to practicability and sensitivity, can be used for tasks as demanding as water-mass tracing.

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