METHODS AND PRINCIPLES OF ANALYSIS FOR TRACE ORGANICS IN WATER

BY

MICHAEL G. JOHNSON, B.App.Sc.

Being a Reading Thesis submitted as
partial fulfilment of the requirements
for the degree of
MASTER OF SCIENCE
UNIVERSITY OF TASMANIA
July, 1985.

CONTENTS

1 INTRODUCTION

The development of methods of analysis for trace organics in water was severely hampered until the introduction, in 1950, by Braus, Middleton and Walton[1] of a large scale sampling system which allowed systematic separation and identification of organic water pollutants. The sampling and concentration techniques available prior to this development restricted the analyst to the use of crude collective parameters, such as biological oxygen demand and total organic carbon or a few methods for specific organic substances such as oil, grease, phenol and furfural, for the measurement of organic water pollutants.[2]

The methods and instruments available for organic analysis became useful in the analysis of organic water pollutants with the introduction of this method. The development in the methods of analysis for trace organics since that time has been closely linked to the development of improved concentration techniques and the rapid development of gas chromatography as a separation technique.

The rapid development in this area is shown by the fact that prior to 1970 only about 100 different organic compounds had been identified in water. Today about 2000 organic compounds have been identified in various waters.

2 CONCENTRATION TECHNIQUES

The trace organic compounds present in a water sample must, in almost every case, be concentrated before analysis. There are several reasons for sample preconcentration. In addition to the low concentration of the compounds present it is also necessary to use instrumental methods of analysis in which only very small volumes, usually in the low microlitre (μL) range, can be used. Many different processes have been used for this purpose of which liquid-liquid extraction, liquid-solid adsorption, gas phase stripping and distillation are the most important. To date no method has been developed that is suitable for the full range of organic contaminants found in water samples. A combination of concentration methods needs to be applied when samples that contain a wide range of substances are to be analysed.

2.1 LIQUID-LIQUID EXTRACTION

Introduction

The simplest and, until recently, most widely used method for the extraction of trace amounts of organic compounds from water has been single step liquid-liquid extraction with a water immiscible solvent. By choosing the correct solvent and other conditions most organic compounds can be extracted

from water.

Principle of the method

Theory:- Solvent extraction is based on the selective distribution of a solute or solutes in two essentially immiscible solbents. The distribution of a component A between the immiscible phases can be considered in terms of the distribution law. At equlibrium the ratio of the concentrations of the solute in the two phases is given by the distribution constant K.

$$K = \frac{\text{total concentration of A in organic phase}}{\text{total concentration of A in aqueous phase}}$$

The distribution of a compound between the two phases is determined by the various attraction and repulsion forces between the solvent and solute. The extraction efficiency depends not only on the distribution constant but also on the volumes of the phases and the number of extractions carried out. It is usual to use a series of extractions since one extraction with a given volume of solvent is less efficient than two extractions using half the solvent volume each time. However, when the distribution constant is large, multiple extractions are usually not required.

Batch Extraction:- Simple one step liquid-liquid extraction using various solvents such as pentane[3-6], cyclohexane[7], hexane[3,8-10], iso-octane[3,5], benzene[10], dichloromethane[10,11], chloroform[12],

methylcyclohexane[3] and benzene/hexane[10] have been described for the concentration of organic solutes from water. A given volume of sample solution is allowed to remain in contact with a given volume of the solvent until equlibrium is obtained. The two layers are then separated.

The method has been applied for extreme trace levels[13,14] when specific detection, eg. electron capture for halogenated hydrocarbons, is available. The sensitivity becomes much poorer when the sample is to be analysed for a wide range of organic compounds due to the fact that the extract must be concentrated by a factor of up to 50,000 before analysis[4]. The extract consists not only of the substances extracted from the water but also of the abundant impurities contained in the concentrated solvent. The accumulation of solvent impurities as well as severe losses of the more volatile extracted substances during concentration often render the procedure impractical.

Grob et. al.[4] and Murray[15] among others have described methods that to some extent overcome this problem. These methods are based on shaking a large amount (1L) of water with a small amount (200µL) of solvent and subsequent high resolution gas chromatographic analysis of the extract without need of further concentration. Using these methods solvent by-products are decreased 500 fold. Qualitative and semi-quantitative information at the parts per billion (10^{12})

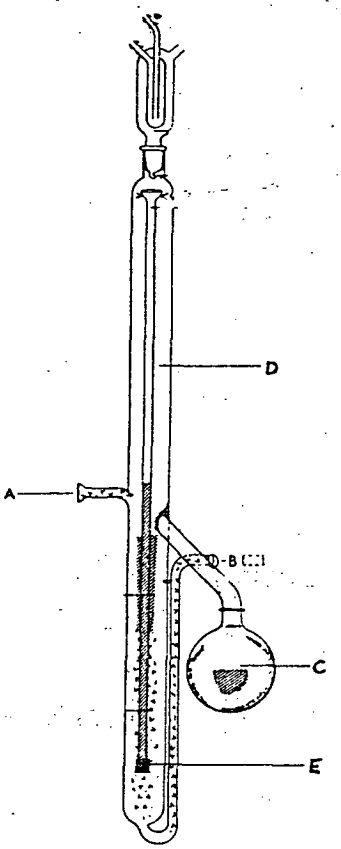
level has been obtained. The use of such small quantities of solvent however, limits the analyst to the use of solvents that have low solubilities in water. The solubilities in water of carbon tetrachloride, carbon disulphide, methylene chloride and diethyl ether for instance prohibits these solvents from use in these methods.[4]

Continuous Liquid-Liquid Extraction:- Werner et.al.[16] first used continuous liquid-liquid extractors for concentrating and isolating trace amounts of organic substances from water. Continuous liquid extraction overcomes two of the limiting factors in solvent extraction. The saturation capacity of the solvent is eliminated by continuously providing fresh solvent and the volume of water available for extraction is not limited as in batch extraction.

In continuous extraction unlike batch extraction the mixing separation and solvent recovery operations are performed in a flowing system. There are three different flow types: countercurrent, crosscurrent and concurrent operations.

Countercurrent Extraction:- The term countercurrent is used to refer to two streams flowing in opposite directions with both phases continually renewed. The types of apparatus used are often based on mixer-settler[17] or column[16,18] operation with large contact surface areas between the two phases. A typical extractor for use with solvent lighter than water is shown

in Figure 1[19].



A - sample inlet
B - sample outlet
C - solvent chamber
D - reflux condensor
E - porous frit.

Figure 1. Countercurrent Extractor design for solvent lighter than water

A concentration factor of up to 10^5 has been obtained with this apparatus.

Crosscurrent Extraction:- The principle of crosscurrent extraction is shown in Figure 2[20].

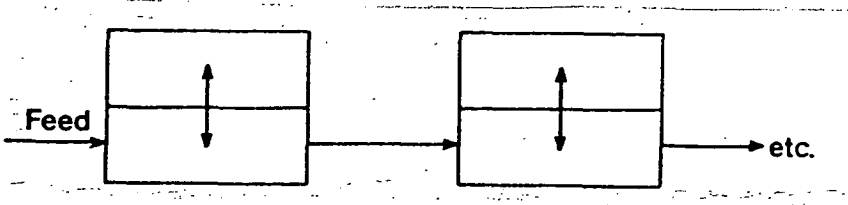


Figure 2. Schematic diagram of cross-current extraction. The vertical arrows indicate introduction of fresh solvent.

Anhoff and Josefsson[21,22] described a continuous liquid-liquid extractor based on this principle. The extraction efficiency ranged between 83-96% for a variety of organic compounds at the 0.1-1.0ng/L level. The apparatus is normally used with a solvent lighter than water but with slight modification it is possible to use a solvent heavier than water.

Concurrent Extraction in a Narrow Tube:- The efficiency of extraction depends on the contact surface area of the two phases, contact time and rate of transport. A very simple method involves the use of a narrow tube in a helical coil. The two phases are pumped through the tube together. Depending on the tube diameter and the surface tensions of the liquids with respect to one another and with respect to the wall of the tube droplets will be formed. The friction between the drops and the wall creates a turbulent flow and therefore mixing. This kind of extractor can be used with either lighter or heavier than water solvents. The phases are separated in a wider column that acts as a settler. This arrangement can be used for both countercurrent and crosscurrent extractions. Wu and Suffet[23] described the use of a 10 metre Teflon helical mixing coil for continuous liquid-liquid extraction of pesticides from water at the microgram (µg)-nanogram (ng)/L levels. The recoveries of these compounds was greater than 80% with an aqueous flow rate of 900 mL/hr and a water to solvent ratio of 10:1.

Concentration of Extracts

It has been shown that the concentration step following liquid-liquid extraction and other techniques such as adsorption onto solids with liquid desorption (see Section 2.2) is a critical step where serious solute losses can occur[24-27]. Junk et al[24] recommend a distillation technique to concentrate the sample after finding that 10-80% of solutes were lost when using free evaporation aided by nitrogen. They used the apparatus shown in Figure 3[24].

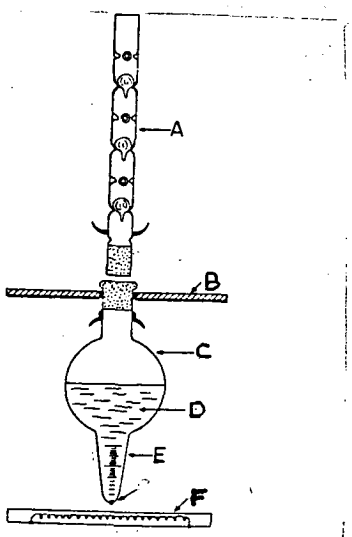


Figure 3. Scale drawing of concentration apparatus (A) Snyder distillation column; (B) bakelite heat shield covered with Al foil; (C) 50ml vessel; (D) solvent; (E) graduated and calibrated taper; (F) hotplate.

Junk et al[24] have also investigated the shape of the vessel in which the concentration step is carried out. Several shapes that were studied are shown in Figure 4[24].

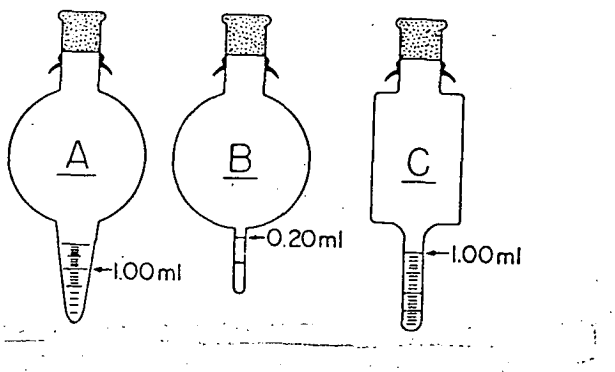


Figure 4. Scale drawing of the concentration vessels. (A) is recommended, (B) is unsatisfactory, (C) is questionable.

When vessels (B) and (C) were used, solute losses from 10-60% noted, whereas losses from vessels of shape (A) were less than 6%.

2.2 ADSORPTION ON SOLIDS

Introduction

Extraction of organic substances from water by adsorption has gained in importance in recent years and appears to be replacing liquid extraction for routine analysis. Activated carbon[1,28-30] has been used widely for several decades and this method has been elaborated in detail and standardised[31]. Recently better results have been obtained by replacing activated carbon with organic resins such as Amberlite XAD-2[32-37], Amberlite XAD-4[37,38], Sephadex[39] and Tenax[37,40].

Principle of Method

Extraction:- Extraction of trace amounts of organic compounds from water with a solid sorbent is a method in which adsorption on a solid substance is used in order to isolate compounds dissolved in water. Like liquid extraction, that is based on the partition of the dissolved compounds between the solvent and the water, sorbent extraction is based on the distribution of the dissolved compounds between the solid sorbent and water. Provided that the sorbent is selected correctly the partition coefficient is shifted more towards the sorbent than in liquid extraction. The principle of the method is therefore analogous to that of liquid extraction, the differences lying in the extraction materials used and in the resulting effect, the enrichment factor.

In the extraction procedure the water sample, typically 1-100 Litres, is passed, usually with the aid of a pump, through a column packed with the solid sorbent. The adsorbed compounds are then desorbed and analysed chromatographically. A typical concentration column[41] as shown in Figure 5, from bottom to top, consists of a porous septum, a layer of sorbent, a layer of glass pellets, a layer of inert material mixed with glass wool and a further layer of glass pellets. The equipment used with this column is also shown.

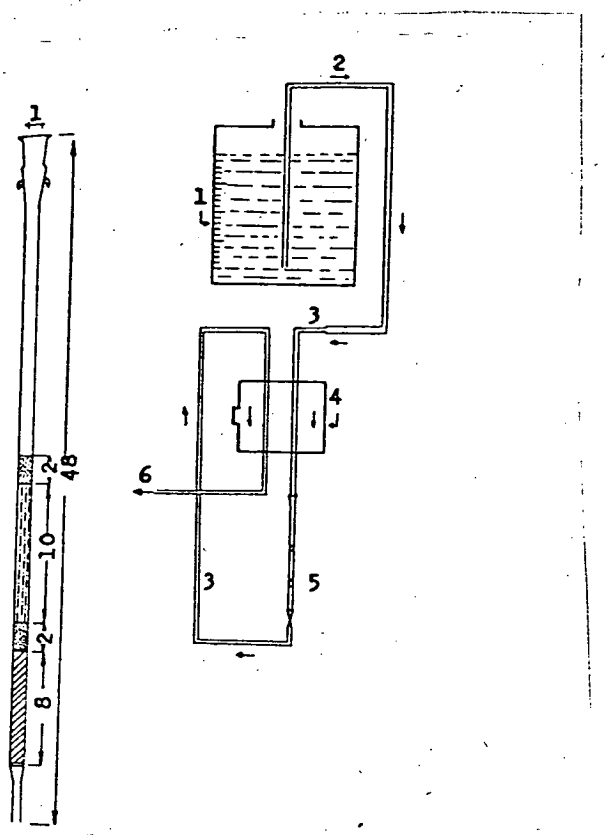


Figure 5. Right: Equipment for extraction. 1 glass container; 2 glass tubes; 3 silicone rubber hose; 4 peristaltic pump; 5 glass adsorption column; 6 extracted water discharge. Left: adsorption column (dimensions in centimetres).

Mineral oils may deactivate the sorbent causing decreased adsorption of compounds of interest. This phenomenon is overcome with the aid of the arrangement described above in which the oils are trapped in the first part of the column[41].

Desorption:- Desorption of the compounds from the concentration column can be performed either with a liquid or by heating.

Liquid Desorption:- When the extraction is completed a small volume of liquid, for which the partition coefficient in the given system is shifted in favour of the eluent (diethyl ether[24,33,42,43], n-hexane[36],

isopropanol[38], methyl isobutyl ketone[44], pyridine[45], acetone[35], chloroform[30]) is passed through the column. As the liquid passes through the column, the adsorbed compounds are desorbed from the column and dissolved in the eluent. The volume of eluent required for total desorption is usually tens of millilitres[24]. As gas or liquid chromatography is used for subsequent analysis only about 0.01 - 0.1% of the total eluent volume (0.1-1µl) can be used for the determination itself. The extract must therefore be concentrated and there is a risk of losses particularly of compounds with lower boiling points if the concentration is performed by evaporation of the eluent[24]. (See section - Concentration of Extracts).

The difficulties with the concentration of the extract are eliminated by using a mini sampler method with as little as 50-100 µL[46] of the eluent being sufficient for desorption.

The presence of the eluent liquid in the solution used for gas chromatographic analysis is another problem encountered when using liquid desorption. A peak due to the eluent is present in the chromatogram and as the eluent is in excess this peak may overlap some peaks of compounds extracted from the water. In some instances the peak of the eluent can be eliminated by using an abstraction precolumn[45].

A method in which a liquid chromatograph[47-50]

incorporates a concentration column before the analytical column of the liquid chromatograph has been described. During the extraction phase water passes through the concentration column while the analytical column is disconnected. When the extraction is completed the concentration column is connected to the analytical column. The adsorbed compounds are desorbed by the carrier liquid and eluted directly onto the chromatographic column.

Thermal Desorption:- Thermal desorption involves the placement of the concentration column before the analytical column of a gas chromatograph. The precolumn is heated and the adsorbed compounds are consequently desorbed and transported by the carrier gas onto the chromatographic column[51,52]. It is important that the desorption temperature and time, which differ for various adsorbents[53], are sufficient to ensure that all of the compounds concentrated on the column are totally desorbed. To eliminate the peak broadening that occurs with this method the first portion of the chromatographic column can be cooled[48,54,55] and only after complete desorption is it heated to the temperature required for the analysis. The temperature of desorption is determined by the stability of the adsorbed compounds and by the maximum temperature at which the chromatographic background of the sorbent is acceptable. The gas chromatograms (Figure 6) obtained by flash heating of Tenax and Amberlite XAD-2 to

400°C and 275°C respectively show that Amberlite XAD-2 is unsuitable for thermal desorption[48].

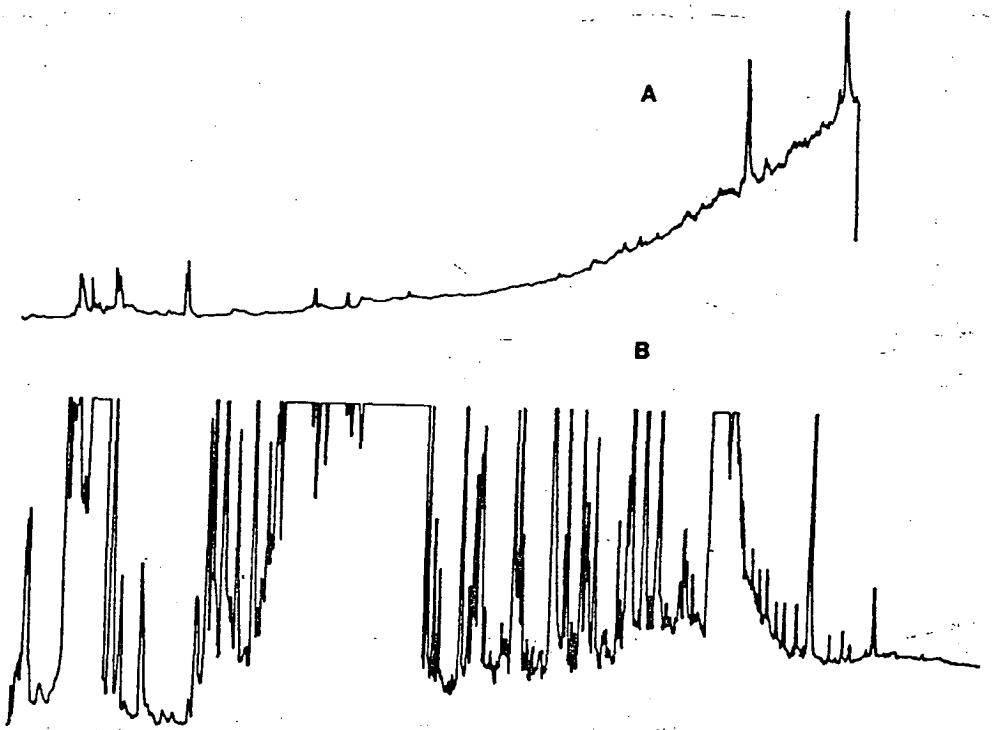


Figure 6. Polymer blanks (A) Tenax, 400°C; (B) Amberlite XAD-2, 275°C.

In thermal desorption, all of the compounds adsorbed from the water sample are transferred on to the gas chromatographic column. This is in contrast to the liquid desorption procedure where a small proportion of the compounds are transferred to the gas chromatographic column. Therefore by using thermal desorption a gain in sensitivity of 2-3 orders of magnitude is achieved, but the entire sample of extracted compounds is consumed in the analysis. A second

advantage of thermal desorption is that volatile compounds are not lost in the extraction and preconcentration steps.

Types of Adsorbents Used

Amberlite Resins: Amberlite resins have received a great deal of attention as adsorbents of organic compounds in water. Four materials are available XAD 2,4,7 and 8. The XAD 2 and 4 resins are polystyrenedivinylbenzene copolymers and are nonpolar, whereas XAD 7 and 8 are polar polymethacrylate resins[32]. Workers that have used amberlite resins have found it essential to use a cleanup procedure similar to one proposed by Stepan and Smith[56], in which the resin is soxhlet extracted from 6 hours with methanol followed by a 6 hour soxhlet extraction with diethyl ether, to remove impurities such as non polymerised material. After the second extraction the resin is equilibrated with 20mL of diethyl ether for 10 minutes and the diethyl ether eluate is analysed by gas chromatography to check the effectiveness of the cleanup. The clean resin is stored under methanol to prevent the resin drying out. It has been shown that dried resin develops cracks which allow more impurities to leach out of the resin[25,57].

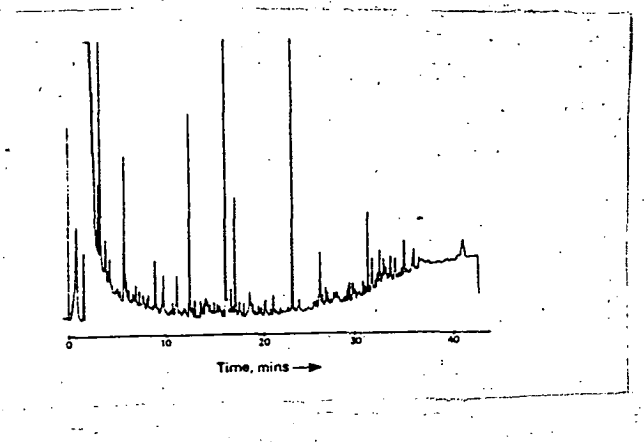


Figure 7. Gas chromatographic scan of the eluent from an XAD-2 blank, after dry storage and dry packing.

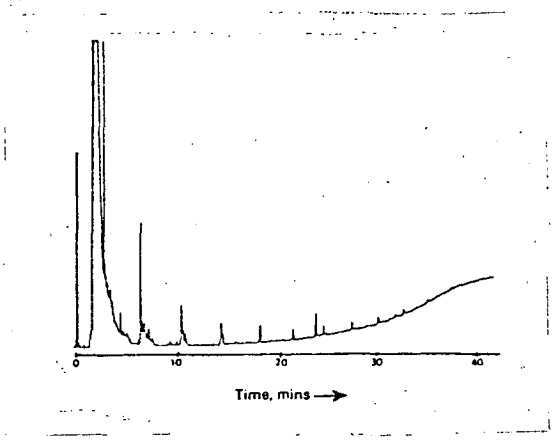


Figure 8. Gas chromatographic scan of the same XAD-2 blank used in Figure 3, but with methanol storage and slurry packing. All other conditions and chromatographic parameters were the same as in Figure 3.

James et al.[58] however, have found it essential to also wash the XAD resin with diethyl ether immediately before used to enable lower detection limits to be achieved due to the absence of interfering compounds such as n-alkanes arising from the breakdown of the resin even when stored under methanol.

The various XAD resins have been used to adsorb

a variety of organic species from water including phenols[35,52], pesticides[36,37,59], poly chlorinated biphenyls[59] and polynuclear aromatic hydrocarbon[60].

The efficiency of XAD-2 in extracting a wide range of organics from water has been studied[24] and a summary of the results can be seen in Table 1.

Table 1: Recovery Efficiency for the XAD-2 Sorption Method

Compound Type	No. Tested	Average % Recovery
Alcohols	8	94
Aldehydes + Ketones	7	95
Esters	15	93
Acids	5	101
Phenols	6	89
Ethers	5	90
Halogen Compounds	10	87
Polynuclear Aromatics	8	89
Alkylbenzenes	4	90
N,S Compounds	10	89
Pesticides + Herbicides	5	90
	Total = 83	Wt. Ave. = 91

Thirteen different chemical classes were tested with four to fourteen chemicals per class. The weighted average of the recoveries was 91% for the 83 compounds tested.

Other studies [61,62] have shown that resin mixtures, in particular an equal weight mixture of XAD-4

and XAD-8, are most efficient when isolating complex mixtures of compounds.

Tenax: Tenax is a porous polymer based on 2,6-diphenyl-p-phenylene oxide. Before use Tenax must be conditioned by heating in a stream of inert gas to 350°C for 30 minutes[48], or for 3 hours with subsequent heating at 200°C overnight[62].

Leoni and Co-workers[40,41] have studied Tenax for the extraction of PAH and pesticides from surface and drinking waters. A diagram of the device used is shown in Figure 5. After the passage of 20L of water (at a flow of 3L/hr.) the column is disconnected and air was blown through for a few seconds in order to eliminate as much water as possible. Pesticides were eluted with three 10mL volumes of diethyl ether. The recovery of pesticides was found to be about 90%[40]. The recovery of Polynuclear Aromatic Hydrocarbons was in the range 85-98%. The main disadvantage of Tenax is that it is very expensive in comparison to XAD resins. This appears to have influenced workers to select XAD resins instead of Tenax.

Activated Carbon: Activated Carbon has been used extensively over several decades[1,28,30,63] as a sorbent for the removal of trace organic compounds from water prior to analysis. The removal of organics from water by carbon is highly dependent upon the polarity of the organic molecule[64]. In general, less polar materials

are adsorbed and recovered more effectively than more polar materials. Before use the carbon must be cleaned. Soxhlet extraction with chloroform for up to 11 hours[61] has been found necessary to obtain acceptable blanks.

One major drawback with the use of activated carbon is the fact that some molecules are irreversibly adsorbed[32,61,65]. It has been shown that carbon adsorption also promotes chemical alteration of some of the organic compounds[66]. Because of these major drawbacks, and the development of other solid adsorbents, the use of activated carbon has declined in recent years. Activated carbon is however still preferred over the more recently developed adsorbents for some applications including pesticide analysis[63].

Polyurethane Foam: Polyurethane foam has been used for the concentration of chlorinated insecticides, polychlorinated biphenyls[67,68] and polynuclear aromatic hydrocarbons[60,69]. The adsorption capacity of polyurethane foam for these compounds was found to be greater than the adsorption capacity of the other solid adsorbents available. The trapped material is usually eluted with methanol acetone or benzene[69].

2.3 HEADSPACE

Static Headspace Technique: The simplest form of headspace analysis involves the sampling and analysis of the vapor phase in equilibrium with an

aqueous sample in a closed container. It has been known for many years that when volatile organic materials in water are allowed to come to equilibrium with the vapor headspace, the concentration in the headspace is proportional to the concentration in the water[70].

Volatile trace organics can be determined in the 2-100μg/L concentration range using this static sampling procedure[8]. The most common way to conduct such an analysis is to partially fill a small vial fitted with a septum cap with the water sample to be analysed. This vial is then placed in a thermostated bath and allowed to come to equilibrium. A sample of the headspace (1-2 mL) is then removed, with a syringe via the septum, for analysis.

Most of the compounds which are amenable to concentration and sampling in this manner are also amenable to gas chromatography. Quantification is obtained by comparing the response of the sample with the response curve prepared by analyzing known concentrations of the compounds of interest added to water.

Temperature, salt concentration, and pH, can all have important effects on isolating volatile trace materials from aqueous samples[71].

Static headspace techniques have been used extensively to determine halomethanes and haloethanes

in water[8,72-74]. One of the major advantages of headspace analysis is that no solvent extraction is involved so that these low molecular weight, volatile compounds are not masked by the solvent peak when analysed by gas chromatography. Detection limits are restricted by the equilibrium concentration of the organics in the vapour phase as well as the limited amount of headspace gas which can be conveniently sampled and analysed. An improved technique using dynamic instead of static sampling has been developed.

Purge and trap technique: Volatile substances present in aqueous samples can be stripped from the water by a stream of inert gas[75-77]. Originally[75] the purged organic compounds were trapped cryogenically. The trapped compounds were then transferred to the analytical system (usually gas chromatography) by rapid heating of the freezing trap. A vast improvement of the recovery was achieved by Grob[29] using an adsorbent trap. The organic compounds were recovered by washing the adsorbent with a suitable solvent. This technique has gained acceptance within the last few years[13,78-81]. A purging device developed by Bellar and Lichtenberg is the most widely used apparatus for the purging step[13]. (Figure 9)

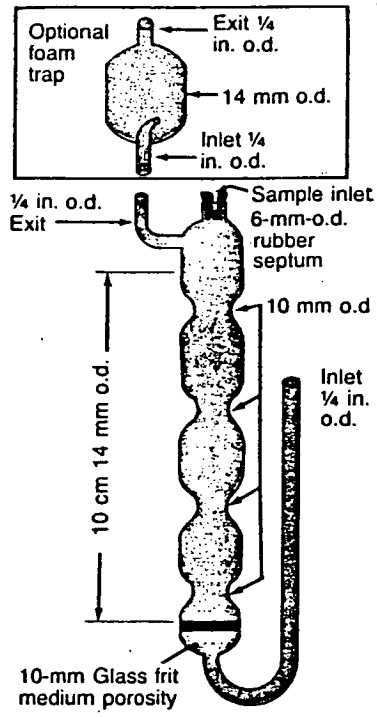


Figure 9 Purging device developed by Bellar

An inert gas, free from volatile organic contaminants is introduced into the inlet. An aqueous sample is then injected into the apparatus. The solid adsorbent trap is connected to the exit of the apparatus. The bubbles of inert gas passing through the frit purge the volatile organics from the aqueous samples. These organics are collected by the adsorbent trap. Purging is continued until the organics are quantitatively removed from the sample and trapped on the adsorbent.

As with static headspace sampling, adding salt, and increasing the temperature of the aqueous sample dramatically improves the removal of most organic compounds[71].

Purge and trap techniques have been used to routinely analyse for organohalides[82,83], arenes, and

vinyl chloride[79] and other volatile organics with boiling points less than 140°C[84] at the 1µg/L level.

2.4 DISTILLATION

Steam distillation can be used as an effective concentration technique for low molecular weight volatile trace organic water pollutants. The technique is quite straightforward.

The sample is placed in a distillation flask and the sample is heated[64]. After distillation the distillate is analysed by a suitable method. Best results have been obtained for those materials which form azeotropes with water that boil at temperatures below 99°C[64].

A small all glass distillation-concentration system for organics in water which can obtain 300 fold concentration with recoveries of 80% has been described[85]. Linear recovery of acrolein, acrylonitrile, alcohols and ketones was reported over the concentration range of 10-100ng/L.

A technique combining distillation and static headspace sampling has been described[86]. Detection limits for methanol, ethanol, acetone, 2-propanol and methyl ethyl ketone were in the range of 4-8ng/L.

An exhaustive steam distillation/solvent extraction apparatus (Figure 10) has been developed[87].

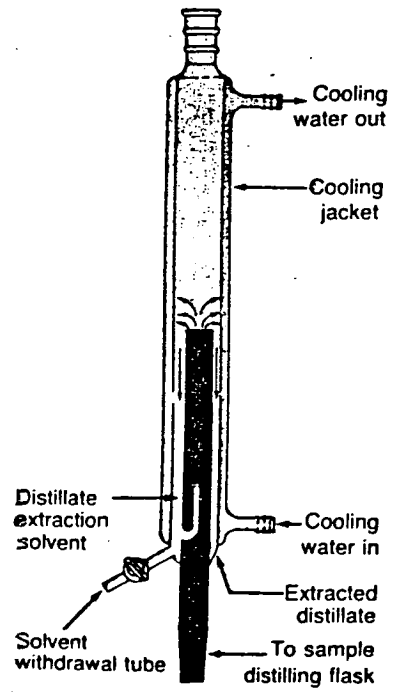


Figure 10 Exhaustive steam distillation and solvent extraction apparatus.

The water sample is placed in a distillation flask fitted to the bottom of the column. The solution is boiled and the steam distillate passes through the inner tube and condenses on the walls of the cooling jacket. The condensate runs down the walls and passes through a layer of low density solvent which extracts the trace organics. The extracted condensate passes through the overflow tube in the centre of the column and returns to the distillation flask. Samples are removed through the solvent withdrawal tube. The apparatus has been limited to pesticide residue analysis to date, but the technique appears to be suitable for other volatile organics as well.

2.5 MEMBRANE SEPARATIONS

Membrane separations can be used to isolate trace organics from water. A membrane is chosen that is permeable to the components of interest but not the undesirable matrix components.

Membrane/Mass Spectrometry: This separation technique is shown in Figure 11. As water containing volatile organic components flows across the surface of a silicon membrane the organics dissolve into the membrane permeate through and enter the mass spectrometer vacuum system where they are analysed conventionally[64,88].

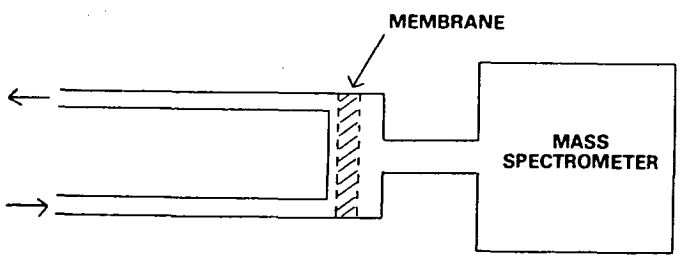


Figure 11 Schematic of Membrane/Mass Spectrometer

When determining several components simultaneously the mass spectrometer is operated in the selected ion mode, choosing ions unique to each species.

Dialysis: The second general type of membrane technique uses dialysis of the components of interest from water into another solvent. Usually the solvent volume is 1-3 orders of magnitude less than the volume

of water[88]. Therefore after dialysis the solute is not only isolated into a more convenient matrix but also concentrated to facilitate analysis.

In some cases dialysis can offer features not obtainable with liquid-liquid extraction. Dialysis can be used with a water miscible solvent; membrane selectivity can prevent removal of otherwise extractable components and solutions that form emulsions can be extracted easily.

2.6 OTHER TECHNIQUES

Other techniques that have been used for concentrating trace organics in water include the following.

Freeze concentration which has been used to concentrate m-cresol 20 fold with an 80% recovery[89-92]. In this technique a portion of the water is frozen which concentrates the dissolved substances in the unfrozen portion.

Lyophilization or freeze drying which has been used as a concentration technique. The water sample is frozen and the water is removed by sublimation under vacuum. The more volatile components are lost in this process. Concentration factors of several thousand have been achieved. A major difficulty is the recovery of the organic material from the residue, which is composed largely of inorganic salts[93].

3 SEPARATION TECHNIQUES

The sometimes large number of organic compounds that are extracted from water samples need to be separated before qualitative or quantitative analysis. The two major separation techniques used are gas chromatography and high performance liquid chromatography.

3.1 GAS CHROMATOGRAPHY

Introduction

Gas Chromatography (G.C.) is the most widely used technique for the separation of mixtures of organic compounds that have been extracted from water. By choosing the correct column and conditions a wide variety of compounds in a mixture can be separated.

Principle of the Method

Chromatography is a process in which chemical species are distributed between a stationary phase and a mobile phase, and migrate in the direction of flow with a certain velocity. The stationary phase in gas chromatography is either a solid (Gas Solid Chromatography) or a thin layer of non volatile liquid held on a solid support (Gas Liquid Chromatography). The mobile phase is an inert gas. A sample containing the solutes is injected into the column where solutes are repeatedly adsorbed by the stationary phase and then desorbed by fresh carrier gas. Each solute travels at its own velocity

and therefore a band of each solute is formed.

Chromatographic Columns

Two basic types of columns are in general use, namely packed and open tubular (capillary) columns. Packed columns are tubes made usually from glass filled with either an adsorbent (GSC) or an inert support coated with a non volatile liquid phase (GLC). They are normally 1-2 metres long and 2-8mm in diameter.

Open tubular columns have an unrestricted hole through which the gas can flow and the separating medium is coated on the wall of the tubing. The major drawback to wall coated open tubular columns (WCOT) is the small amount of liquid phase that the wall is capable of holding. This objection is overcome by increasing the surface area of the column by coating the wall with a finely divided support on which a much larger amount of liquid phase can be coated. This is the support coated open tubular column (SCOT). The main advantage of open tubular columns is that the low pressure drop of the carrier gas along the column allows longer lengths to be used. Open tubular columns range from 30-300 metres long and 0.1 to 0.6mm in diameter.

The separating ability per metre of an open tubular column does not differ greatly from that of packed columns. The use of longer column however, allows separation of compounds that have small differences in

their physical characteristics as well as for the analysis of complex samples Figure 12[94].

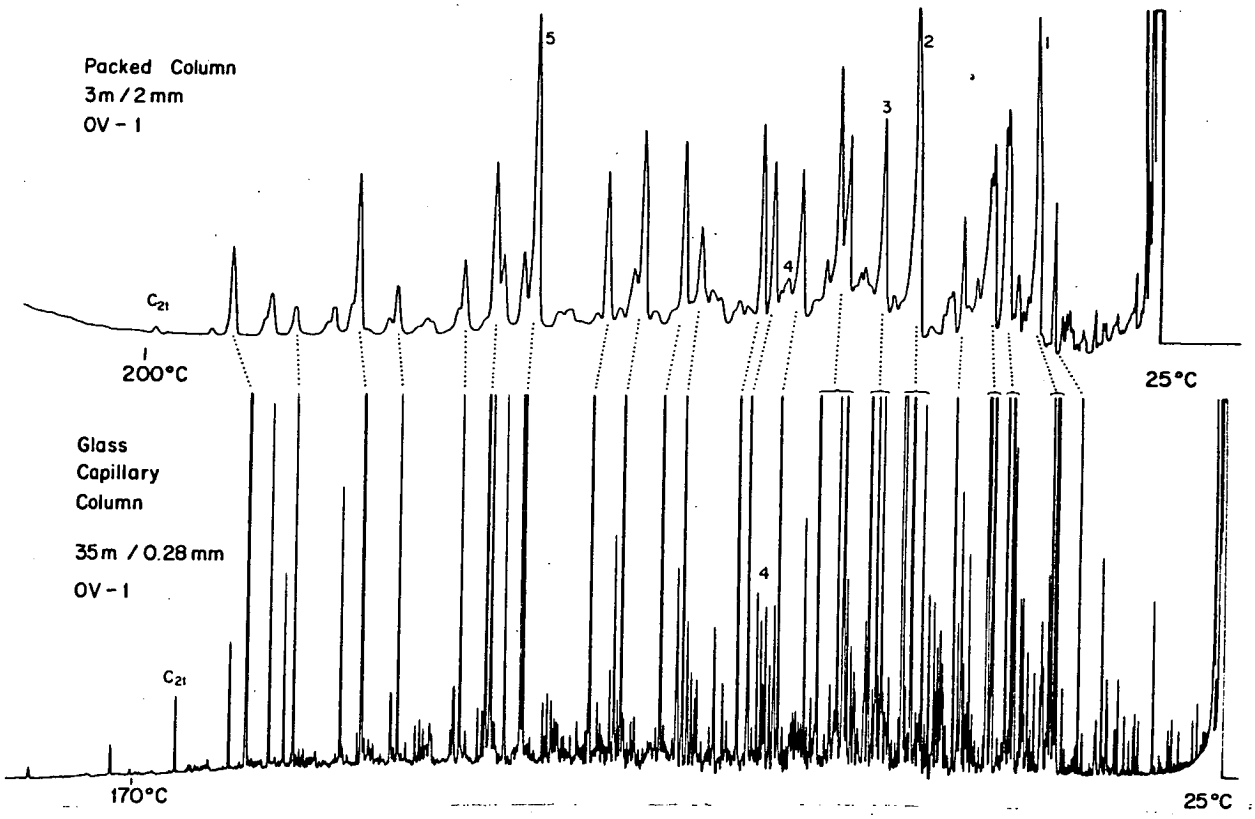


Figure 12 Comparison of packed & open tubular capillary columns.

Detectors

The detector which is located at the exit of the column senses the arrival of the separated components as they leave the column and provides a corresponding electrical signal which is fed via an electrometer to a chart recorder. There are several detection systems available for use and although the fields of application

of each detector overlap to a certain extent one of the detectors will usually have characteristics making it most suitable for a particular analysis.

The characteristics of the three most common detectors used in the analysis of trace organics in water are listed below.

Type of Detector	Selectivity	Detection limit (g)	Applications
Flame Ionisation Detector	all organic compounds except formaldehyde and formic acid	1×10^{-9}	organic acids[95] phenols[96] polynuclear aromatic hydrocarbons[39] samples containing a wide variety of pollutants[94,97,98]
Electron Capture Detector	compounds having a high affinity for electrons (halogen containing compounds)	1×10^{-12}	organohalogen compounds in wastewater[99] polychlorinated biphenyls in drinking water[100] chlorophenols in drinking water[101] phenols after conversion to their heptafluorobutyrl derivatives[102]
Thermionic Specific Detector	compounds containing nitrogen or phosphorus	N: 1×10^{-10} P: 5×10^{-11}	hydrazine residues in water[103] nitrogen containing pesticides[138]

3.2 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

Introduction

The application of high performance liquid chromatography (hplc) to the analysis of trace amounts of organic compounds in water has gained importance in recent years. Typically 80-90% by weight of the organic components of a water sample will not, even after derivitization, pass through a gas chromatographic column. High performance liquid chromatography is presently the leading technique for separating these non volatile compounds.

Principle of the Method

As in gas chromatography, high performance liquid chromatography is a process in which separation of chemical species is achieved by partitioning between mobile and stationary phases.

In hplc eluent from a solvent reservoir is filtered, pressurised and pumped through the chromatographic column. A mixture of solutes injected at the top of the column is separated into components on travelling down the column and the individual solutes are monitored by the detector and recorded as peaks on a chart recorder.

In hplc unlike gc selectivity is achieved by varying the mobile phase as well as the column packing. Hplc columns may be run isocratically i.e. constant

composition of eluent or they may be run in the gradient elution mode in which the mobile phase composition varies throughout the run. Gradient elution is the analogue of temperature programming in gc.

The main mode of chromatography used is adsorption chromatography. In adsorption hplc the separation is carried out with a liquid mobile phase and a solid stationary phase which reversibly adsorbs the solute molecules. The stationary phase may be polar (silica) with a relatively non-polar mobile phase (hexane) as has been used for the analysis of phthalate esters at the ng/L level[105] or non-polar with a polar mobile phase. The latter is known as reverse phase hplc. Reverse phase hplc has been used for the analysis of phenols[106,107], polynuclear aromatic hydrocarbons[50], pesticides[108] and tetrachloroethylene[109].

Detectors

After leaving the column the individual solutes are monitored by the detector and recorded as peaks on a chart recorder.

Ultraviolet detectors: UV detectors measure the change in UV absorption as a solute passes through a flow cell. On modern instruments the flow can be stopped and a scan of the UV spectrum can be made for each solute. The sensitivity of the UV detector depends on the molar extraction coefficient of the solute. Phenols[106], phthalate esters[105], tetraphthalic acid[110],

pesticide residues[108] and tetrachloroethylene[109] have all been determined at the ng-μg/L levels by hplc using UV detection.

Fluorimetric Detectors: As the solute passes through a flow cell it is excited by UV radiation of a given wavelength. The fluorescence energy which is emitted at a longer wavelength is then detected. Fluorimetric detectors are generally more sensitive than UV detectors. Polynuclear aromatic hydrocarbons (PAH) have been determined using fluorimetric detectors[50,111,112] as low as the subpicogram per litre level[111].

Refractive Index Detectors and Infra-red Detectors: These are available but have not been widely applied to the determination of trace organics in water because of their lower sensitivity.

Mass Spectrometry: Combined high performance liquid chromatography mass spectrometry has been used for the determination of herbicides[139] and pesticides[140] but its application has been limited by low sensitivity.

4 IDENTIFICATION TECHNIQUES

The major techniques that have been applied to the identification of organic water pollutants are mass spectrometry and infra red spectroscopy.

4.1 MASS SPECTROMETRY

Introduction

The first mass spectrometer was developed around 1912. However, it was not used for the identification of water pollutants until much later[113]. The coupling of a gas chromatograph to a mass spectrometer provided a technique of first separating and then identifying components in a mixture[114]. One of the most significant advances in the identification of water pollutants came with the development and application of computer assisted gas chromatography/ mass spectrometry which allows computer matching of sample spectra with reference spectra in data banks[115].

Components of Mass Spectrometers

The mass spectrometer is a device with the ability to produce charged particles consisting of the parent ion and ionic fragments of the original molecule and separate them according to their charge to mass ratio. There are four basic elements in a mass spectrometer:- the inlet system, the ion source, the mass separator and

the ion current detector.

Inlet System:- In the analysis of water pollutants, the mass spectrometer is almost invariably used coupled to a gas chromatograph. The normal inlet system of the mass spectrometer, which is capable of accepting solid, liquid or gaseous samples, is replaced by a gas chromatograph-mass spectrometer (GC-MS) interface. The purpose of the interface is to eliminate the carrier gas. Several interfaces have been described[116]. With the advent of vitreous silica capillary gas chromatography columns with much lower carrier gas flows and the improvement of vacuum systems of mass spectrometer, the direct coupling of the GC column to the ion source of the mass spectrometer has been possible. A brief survey of the most common coupling techniques is given in Figure 13.

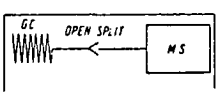
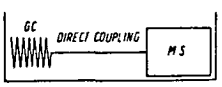
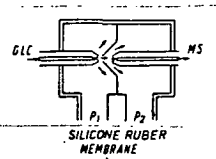
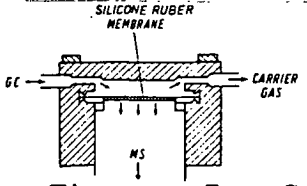
Type of Interface	Flow Range mL/min	Efficiency %	Enrichment Factor
a 	1-100	1-90	-
b 	10	100	-
c 	10-80	50	50
d 	1-50	90	10^4

Figure 13 Schematic Survey of interfacing techniques used in GC-MS. a) Open Split; b) Vacuum Coupling; c) Jet Separator; d) Membrane Separator.

The enrichment factor is defined as the relative increase in the concentration of the compound in the carrier gas after passing the interface. The efficiency is the percentage of the compound in the GC effluent entering the mass spectrometer.

More recently an interface has been developed which allows a liquid chromatograph to be linked to a mass spectrometer[117]. Although still in the developmental stages this technique has been applied to organic water pollutant analysis[118].

Ion Sources:- The most common ion source is electron impact ionisation, where positive ions are formed by bombarding the sample with electrons emitted from a heated filament. Chemical ionisation, where a reactant gas is fed into the ionisation chamber during electron bombardment produces a spectrum where, unlike electron impact ionisation, the molecular ion is often the most prominent. Field ionisation, where molecules produce positive ions when subjected to intense electric fields, produces a simpler spectrum than electron impact but has the disadvantage of needing much more sample. Each ionization process produces molecular ions and a number of ionic fragments. The mass spectrum produced is a record of the numbers of different kinds of ions and is characteristic for every compound, including isomers. This is the basis for the application of mass

spectrometry in the identification of organic compounds. The positive ions formed in the ionization chamber are accelerated by an electrostatic field into the mass separator.

Mass Separator:- The primary function of the mass analyser is to separate the positive ions from the ionization source according to the mass to charge ratios with either electrical or magnetic fields. The mass separator must be capable of focusing the ion beam to improve separation between adjacent positive m/e ions for more accurate and precise mass measurements. Although there are many types of mass analysers available, the magnetic-deflection cycloidal focusing, double focusing, time of flight and quadrupole analyzers are the most commonly used.

Ion Current Detection:- After leaving the mass analyzer the separated ions strike a collector. For ion currents above 10^{-15} Amps an insulated cup (Faraday Cage) is used for the collector. As each positive ion strikes the collector it picks up an electron so that an electron current flows to the collector. For ion currents below 10^{-15} Amps an electron multiplier is used.

Applications

Combined gas chromatography/mass spectrometry is the most advanced method for the separation and

identification of trace organics in water. The technique has been used widely during recent years. Examples of its application are, the identification and determination of purgable organics in wastewaters[119], chlorinated guaiacols[120], phenolics, pesticides and polychlorinated biphenyls[121], and chlorinated phenols[66].

Specialized computer programs have been developed to simplify the data processing and to extract obscured information from the data obtained in a GC/MS run. One such computer program has received various names in the literature, "Limited Mass Search", "Specific Ion Monitoring" or "Mass Chromatography". The technique is used to identify the locations of specific compounds or classes of compounds within a total ionization chromatogram (TIC). The computer program extracts the ion current intensities from each spectrum in the TIC at a specific mass which is characteristic of a compound or class of compounds. This technique has been used for the determination of phthalate esters[122], polynuclear aromatic hydrocarbons[123], mononuclear aryl hydrocarbons[124], chlorinated organics[125] and many other types of compounds in water extracts.

4.2 INFRARED SPECTROSCOPY

Introduction

Infrared spectroscopy has been used for many years as a method of identification of organic contaminants

in water[28,126]. The past few years have seen considerable interest in the use of combined gas chromatography and infrared spectroscopy (GC/IR) due to the advent of Fourier Transform infrared spectroscopy (FTIR). Computer software has been developed which enables real time infrared reconstructed chromatograms and on line library searching[127,128]. This should greatly increase the utilization of GC/FTIR for environmental water analysis.

Instrumentation

Fourier transform infrared spectroscopy measures the interferogram resulting from a Michelson Interferometer (Figure 14).

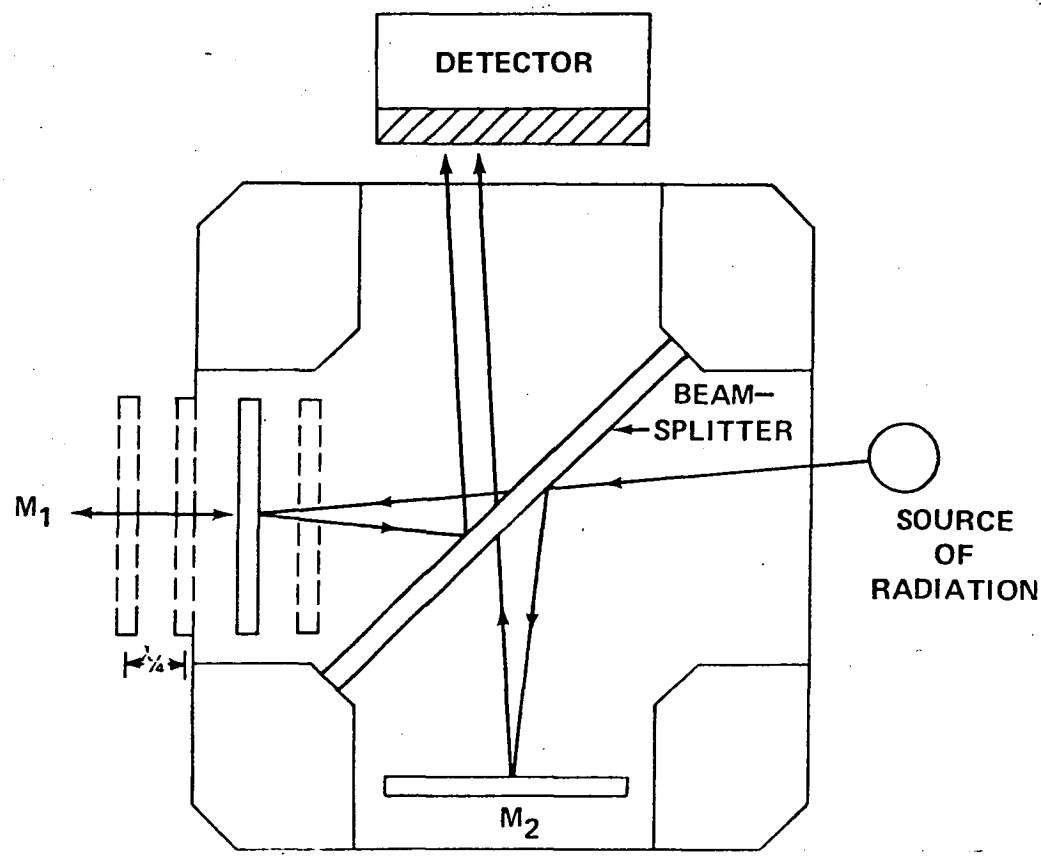


Figure 14 Schematic of Michelson Interferometer

An interferometer consists of a beam-splitter, a fixed mirror and a moving mirror. The beam of light is split so that half of the light goes to each mirror. As the moving mirror (M_1) goes back and forth the two split beams are recombined with one beam being out of phase with the other. A beam of light resulting from the constructive and destructive interference of the two split beams is produced and directed to the sample cell. The light transmitted through the sample strikes the detector.

After the data are collected a computer executes a Fourier Transform of the data into a single beam spectrum which may then be ratioed against a background to produce a customary transmittance Vs wavenumber spectrum.

There are two major advantages of FTIR over dispersive instruments.

An FTIR instrument has a much higher signal to noise ratio than a dispersive instrument due to the fact that all frequencies simultaneously reach the detector. This is known as Fellgett's advantage[129,130].

All energy that reaches the detector of a dispersive spectrometer must pass through the narrow entrance and exit slits of the monochromator. The interferometer has a large circular aperture and no slits therefore more energy reaches the detector resulting in greater sensitivity. This is known as Jacquinot's advantage[131].

Applications

These advantages and the development of sample cells (light pipes) and transfer lines to allow the on-the-fly analysis of components separated by capillary chromatography[132,133] has allowed the technique to be widely used for the analysis of trace organics in water. GC/FTIR has been used to identify up to 55 substances in the one sample[134]. GC/FTIR has been successfully used to identify components in paper mill wastewaters[133,135]. The use of FTIR to identify peaks eluting from a HPLC has also been investigated[136] but there has been little application of this method to water analysis.

GC/FTIR like GC/MS is used almost entirely for the identification of unknown compounds in complex mixtures. Studies show that the two techniques are complementary[137]. GC/FTIR shows more selectivity for polar compounds, whereas GC/MS selectively favours non-polar compounds.

5 CONCLUSION

The rate of development in the area of analysis of trace organics in water is still limited by the available methods for separating the compounds from water and from each other. As yet there is no technique that is applicable to the full range of contaminants that are encountered.

XAD resin adsorption appears to be the best technique for separating organic contaminants from water but not all compounds encountered can be quantitatively desorbed from the resin.

Most of the work on separation techniques to date has dealt with the small percentage of compounds that are volatile and are capable of being separated by gas chromatography. New techniques will need to be developed for the remaining compounds. Much wider use of liquid chromatography/mass spectrometry could solve some of these problems.

The area of identification of organic pollutants should see wider use of gas chromatography/Fourier Transform infrared spectrophotometry as these instruments become more freely available. This technique will complement the information gained by the use of gas chromatography/ mass spectrometry. There may also be contributions from little used techniques such as nuclear magnetic resonance.

There should be continued concentrated research in the area of identification of trace organics in water over the next few years.

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