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THE ANALYSIS OF ORGANIC COMPOUNDS IN SEAWATER, 1978-1983

B.G. Whitehouse, C.C. Parrish and P.J. Wangersky

REPORT 9
NRCC No. 23609

Marine Analytical Chemistry Standards
Standards de chimie analytique marine

National Research Council Canada
Conseil national de recherches Canada

MARINE ANALYTICAL CHEMISTRY STANDARDS

In 1976, the National Research Council of Canada established a program in support of analytical chemistry aspects of marine science. A recommendation to do so had been made by the Canadian Committee on Oceanography at its 62nd meeting in June, 1975.

In this program, the National Research Council seeks the continuing advice of a Committee on Marine Analytical Chemistry representing chemists active in research on analytical chemistry and of government, university and commercial laboratories applying analytical chemistry in marine science. Further information about this Committee is on the inside back cover of this report.

National Research Council staff at the Atlantic Research Laboratory, Halifax, N.S., and the Division of Chemistry, Ottawa, Ontario, work in support of this program. Much is done in cooperation with other laboratories and through contracts. The results are published in the scientific literature and in this series of reports.

Correspondence should be addressed to Dr. H. A. Gillis, Secretary, Committee on Marine Analytical Chemistry, Office of the Atlantic Regional Director, National Reserach Council, 1411 Oxford Street, Halifax, NS B3H 3Z1.
Telephone: (902) 426-8070.

STANDARDS DE CHIMIE ANALYTIQUE MARINE

Le Conseil national de recherches du Canada a crée en 1976 un programme
visant à développer certains aspects de la chimie analytique liés aux sciences de
la mer. Cette décision donnait suite à une recommendation faite par le Comité
canadien d'océanographie lors

Dans le cadre de ce pro es a mis sur
pied un Comité permanent de des chimistes,
qui effectuent des recherche es
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aux sciences de la mer. Vo au sujet de
ce comité à la troisième pag

Le personnel du Consei e recherches
de l'Atlantique, situé à Ha a chimie,
situé à Ottawa (Ontario), t mme. Une
bonne partie du travail de tres
laboratoires et par voie de s sont publiés
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THE ANALYSIS OF ORGANIC COMPOUNDS IN SEAWATER, 1978 - 1983

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ABSTRACT

The marine organic analytical literature was reviewed for the period 1978-1983, and the earlier NRC report on the analysis of organic compounds in sea water (Wangersky and Zika, 1978) brought up to date. Particular attention was paid to some classes of compounds, such as the hydrocarbons, which were not fully covered in the original publication, and to those methods, such as supercritical fluid chromatography, which are still in the development stage.

RESUME

Une revue de la littérature concernant la chimie marine, organique el analytique, couvre la période 1978-1983, et le précédent rapport CNR, portant sur l'analyse des composés organiques dans l'eau de mer (Wangersky and Zika, 1978) est mis à jour.

Certaines classes de composés, tels les hydrocarbures qui n'étaient pas couverts à fond dans la première publication, font l'objet d'une attention particulière. Tel est aussi le cas pour certaines méthodes encore en développement, comme la chromatographie fluide supercritique.

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--THE ANALYSIS OF ORGANIC COMPOUNDS IN SEAWATER--

1. INTRODUCTION

In this report we propose to update the Wangersky and Zika (1978) report, "The Analysis of Organic Compounds in Seawater". The format of the present report will in some respects be similar to that of its predecessor; however, references and discussions contained in Wangersky and Zika (1978) will not be repeated here unless necessary.

Unlike its predecessor, the body of this report will be divided into two main sections: (i) The analysis of operationally defined fractions, and (ii) The analysis of specific chemical classes and compounds. We have placed these fractions under separate headings for two reasons: (i) Some of the organic matter may exist in more than one of these operationally defined fractions, and thus it may be confusing to discuss them independently, and (ii) We wish to emphasize that the analytical or sampling technique itself defines the fraction.

The emphasis upon particular compounds or groups of compounds is not altogether a matter of choice; there are fads in science, as there are in any other human activity, and any given five-year period will see an emphasis on some areas of analysis and an apparent stasis in others. In the past five years, the use of hydrophobic resins as collectors and concentrators of organics from solution, as well as the improvements in HPLC, has resulted in a large body of work on lipids, while carbohydrate and protein analysis has languished somewhat.

Although organic matter in seawater is quantitatively rather uniform (concentrations range from approximately 0.5 to < 2.0 mg

C/l), it is qualitatively complex. Most major classes of organic compounds can be found in the marine environment. In addition to the well-defined compounds, ill-defined complex polymeric material can also be found in seawater. Actually the majority of marine organic matter is as yet poorly defined. The situation is further complicated by the fact that marine organic matter does not exist in a single phase. That is to say, at environmental conditions organic matter has been found in the liquid, solid, and gas phase. Poorly defined filter characteristics have impeded investigations of partitioning between truly dissolved and solid phases, especially with respect to organic material in the colloidal size range.

In marine chemistry it is important to realize that a class or fraction of organic matter representing a small percentage of the total concentration is not necessarily insignificant; on a qualitative basis it may be of fundamental significance. In addition to such fractions as the volatile organic matter, this statement also applies to specific compound classes. These classes are chemically defined; thus it is not surprising that there are often specific and accurate techniques available for their analysis. However, problems arise in finding sampling and separation procedures which do not cause significant contamination or loss of the organic compounds of interest.

In the discussion that follows, analytical problems discussed by Wangersky and Zika (1978) and those outlined above will become evident. The marine analytical chemist has travelled a long way since the Challenger expedition; however, the journey is far from over. We must continue to strive for direct and 'real-time' procedures which are not biased by the acts of sampling and analysis.

2. THE ANALYSIS OF OPERATIONALLY DEFINED FRACTIONS

From a standpoint of analytical chemistry, it is very difficult to devise an accurate analytical procedure for substances of unknown or ill-defined chemical character. This has caused the aquatic environmental chemist to venture into a realm that pure chemists righteously avoid, the realm of operationally defined 'fractions' of organic matter. An operationally defined fraction is one defined by the particular sampling and analytical techniques employed to collect and analyze it. Such operationally defined fractions include gelbstoff, humic substances, dissolved organic matter, particulate organic matter, and volatile organic matter.

In order to compare data of operationally defined fractions it is necessary that the scientists involved use the same sampling and analysis procedures. As this report will demonstrate, this has not always been the case in marine organic sciences. An example is the study of marine volatile organic matter, which now has almost as many operational definitions as there are researchers in the field.

In this section we discuss the analysis for total organic matter (TOM), dissolved organic matter (DOM), particulate organic matter (POM), and volatile organic matter (VOM). The analyst may just wish to quantify these fractions rather than investigate their composition, and thus may analyze for total organic carbon (TOC), dissolved organic carbon (DOC), particulate organic carbon (POC), and volatile organic carbon (VOC). We will also discuss humic substances.

The actual operational definitions are quite simple. DOM is that which passes through a filter, whereas POM is that which is retained. The original definition involved 0.45 µm membrane filters; however, various glass fibre filters have since become popular. In fact, many aquatic scientists now apply the terms to whatever type of filter they are employing. Such deviations from the original operational definition are generally overlooked, probably for the reasons that in many cases there is little alternative, or that the 0.45 µm definition is just as inadequate. VOM is that which can be removed by gas phase bubbling at a given temperature.

TOM is the sum of the DOM, POM, and VOM. Therefore the TOM theoretically contains all of the organic matter in seawater, including the individual compound classes. However, all of the methods available for the analysis of TOM or DOM lose some of the VOM during sample preparation. This can lead to qualitative problems, but is probably quantitatively insignificant; recent reports indicate that the VOC represents less than 0.1% of the TOC (see section on VOM).

Humic substances may exist in both dissolved and colloidal form, and thus may be found in both the DOM and POM fractions. The operational definition(s) of humic substances is reserved to later in this section.

2.1 TOTAL AND DISSOLVED ORGANIC MATTER

The major advances that have been made in the analysis of TOM and DOM since the Wangersky and Zika (1978) review have not been in the development of new analytical methods; they have been in the evaluation of the accuracy of available techniques, with the subsequent emergence of a preferred procedure. A factor in this advancement was the development of a dry oxidation method for the analysis of TOC in seawater which was precise and accurate enough to be used as a method of reference (MacKinnon, 1978). The method involves acidification, followed by evaporation under vacuum, and combustion of the dried salts in a high temperature furnace. Although precise and accurate, the technique is not suitable for routine analysis as it is time consuming and requires considerable skill on the part of the operator.

Gershey et al. (1979) presented an intercomparison of three oxidation methods used for the analysis of DOC in seawater, with MacKinnon's TOC method being used as the reference technique. They concluded that the high temperature oxidation and photo-oxidation methods gave results which differed by less than 5%, whereas the persulphate oxidation results were approximately 15% less than those found by the high temperature method. The photo-oxidation method blank value of < 0.02 mg C/l was superior to that of the dry combustion (< 0.1 mg C/l) and persulphate oxidation (approximately 0.2 mg C/l). The mean coefficient of variation of replicate analyses was 2.65% for the dry combustion method, 2.9% for photo-oxidation, and 5.4% for persulphate oxidation.

Although slightly less efficient than the dry combustion TOC method, the photo-oxidation method for DOC analysis emerges as the preferred technique as it requires minimal operator skill and has the potential for producing 'real-time' data. The majority of the available methods for the analysis of DOC in seawater by photo-oxidation are based upon the automated method presented by Collins and Williams (1977). They purged the acidified sample to remove inorganic carbon, and then UV photo-oxidized the organic matter to CO_2. The gas was then quantified by a nondispersive infrared analyzer (NDIR). The lower limit of sensitivity of their method was governed by the blank. Gershey et al. (1979) significantly improved the sensitivity by omitting the persulphate oxidizing agent and borate buffer. They found that their modification of the Collins and Williams (1977) method did not quantitatively oxidize the sulphur-containing compounds, but concluded that this should only create problems with samples collected from anoxic environments. Blazka and Prochazkova (1983) found that the addition of persulphate increased the yield of some compounds but decreased the yield of others. They concluded that maximizing the performance of the UV lamp was a more reliable method of improving oxidation than the addition of oxidants, buffers, or catalysts.

Although the UV photo-oxidation method has been automated and developed to a sufficient level of precision and accuracy, the question still remains as to whether it can be operated at sea in order to obtain continuous real-time data. Mueller and Bandaranayake (1983) concluded that their modification of the Collins and Williams (1977) photo-oxidation method could be operated at sea. On the other hand, Wangersky and Whitehouse (1980) concluded that the Gershey et al. (1979) modification of the Collins and Williams (1977) method had significant problems when operated at sea. The type of ship used and the sea conditions encountered during operation may be a major cause of this apparent discrepancy. Wangersky and Whitehouse (1980) found that the main problem was vibration caused by the ship's engines, resulting in excessive baseline noise. Ship movement was a problem only during sea conditions rough enough to prevent or limit the collection of samples. Other problems encountered by Wangersky and Whitehouse when analyzing for DOC at sea have been eliminated by Mantoura and Woodward (1983). Mantoura and Woodward (1983) modified the Collins and Williams method by utilizing a pair of thermostatically controlled fans to cool the photo-oxidation chamber, and by installing a second UV radiation coil in order to obtain purified water for washes and blanks. Another potential improvement to this system may be to enclose the sample chamber and purge it with purified oxygen (Blazka and Prochazkova, 1983), thus isolating the sample rack from contaminated ship air.

The problem of excessive baseline noise from the NDIR analyzer which was encountered by Wangersky and Whitehouse (1980) may not be present in modern NDIR analyzers or other types of CO_2 analyzers. For example, Safranko et al. (1983) discuss a NDIR analyzer that does not suffer from the problem of chlorine gas corrosion of the optical system, and has improved electronics for controlling baseline noise and drift. An automated coulometric titration detector for CO_2 gas that should be less responsive to ship vibrations than a NDIR analyzer is also commercially available (Wangersky, 1981). Schreure (1978) used a colorimeter to detect the CO_2 produced by the photo-oxidation of DOM in seawater. The limit of detection was 0.1 mg C/l with a coefficient of variation of 5.2% (10 standard samples of 1 mg C/l).

The photo-oxidation method has significant problems and may not be the ultimate answer to the question of DOC analysis in seawater; other approaches may prove to be superior. For example, Salonen (1979) has reported a direct injection technique for TOC analysis. It involves placing or injecting the sample directly into a high temperature combustion chamber followed by NDIR analysis of the CO_2 gas. This technique is certainly preferred over methods requiring considerable sample manipulation prior to combustion. A potential problem with the method is that it uses small sample volumes, and thus would require a very sensitive detector when analyzing oceanic samples.

The perfection of DOC or DOM analysis by direct injection chromatography would add a new dimension to the field. Chromatographic adsorbents could concentrate the DOM and provide qualitative information by fractionating the DOM according to chemical and physical characteristics (Gloor and Leidner, 1979; Melcher and Caldecourt, 1980; Grob and Habich, 1983; Zlatkis et al., 1983). Such information could prove to be valuable in the study of variability and flow of organic matter in aquatic systems. Problems associated with this approach include limited sample volumes and interference by water. Leenheer (1981) has reported a multi-resin extraction and fractionation procedure for terrestrial DOM. As expected, resin bleed resulted in blank values that would be prohibitive for oceanic samples.

2.2 PARTICULATE ORGANIC MATTER

In their report, " The Analysis of Organic Compounds in Seawater", Wangersky and Zika (1978, pg 45) stated that "The real problems in POC determinations are not in the analyses, but in the sampling and sample handling end of the procedures". This statement is as true today as it was five years ago. The CHN analyzer discussed by Wangersky and Zika (1978) is still the preferred method for POC analyses; thus we refer the reader to the Wangersky and Zika (1978) report for further discussion of POC analyses. For examples of the analysis of POM for specific organic compounds we refer the reader to Wakeham (1982) and references cited therein. The subjects of sampling, analyzing oceanic POM, and particle dynamics have also been reviewed recently by Simpson (1982). The present report will focus upon the sampling and sample handling procedures that are currently employed for POM.

The classical method for collecting seawater samples is with a water sampling bottle. Although Gordon et al. (1979) realized that there was a possibility of not sampling the rapidly settling particles, they considered their 5 l and 12 l Niskin bottles as being suitable for POM sampling. In light of other recent observations, this statement can be challenged. In addition to the problem of the retention of rapidly settling particles below the side mounted sampling spigot of a Niskin bottle, there may be a problem with the drawing of sample through the spigot itself. Gibbs and Konwar (1983) reported that such sampling procedures are unacceptable for determining the concentration and size of flocculent particles because the flocs coming out of the bottle are 0.5 to 0.2 times the size of the flocs inside the bottle. Changing the size of a particle may affect its filter retention, thus possibly affecting POC concentration. There is an additional problem of large particles not being collected by Niskin bottles (Knauer et al., 1982). Although these large particles are relatively rare, they are significant with respect to transport of organic matter through the water column (Iseki, 1981; Simpson, 1982).

The majority of researchers using Niskin bottles for sampling POM use the 30 l bottle. The larger diameter of this bottle could conceivably reduce the effect of the sampling problems. The larger bottle may also collect a sufficient amount of water to allow sampling in regions of low POM concentration. If the sampling spigot is bottom mounted instead of side mounted, bottle effects could be further reduced.

POM is usually separated from bulk seawater by filtration. Oceanographers have been aware of significant problems resulting from the use of filters for quite some time (Wangersky and Zika, 1978). However, a problem that has recently pushed its way to the forefront is that of sampling colloidal organic matter. Our present definition of DOM and POM result in the possibility of colloids (0.001 to 1.0 µm) residing in both the DOM and the POM. Although it has long been recognized that glass fibre filters may adsorb significant amounts of DOM, it is now being questioned whether this adsorption problem is due to truly dissolved organics or due to the entrapment of colloidal organic matter (Bishop and Edmond, 1976; Cauwet, 1978; Bates et al., 1983; Young and Cline, 1983). The potential magnitude of this problem is emphasized by several recent reports (Cauwet, 1978; Herbland and Le Bouteiller, 1981; Yentsch, 1983) which indicate that a significant percentage of the organic matter considered to be 'dissolved' at present may actually be in colloidal form. As the amount of 'dissolved' organic matter in a given seawater sample is in general considerably greater than the amount of 'particulate' organic matter (mg C/l compared with µg C/l), the inclusion of even a small percentage of the 'DOM' into the 'POM' fraction could extensively alter our view of the concentration of oceanic organic matter in the solid phase.

We are inevitably trapped by semantics in our discussions of the distribution of organic carbon between the dissolved and particulate phases; our definitions leave us with the impression that a hard-and-fast line can be drawn between the two phases, with all of the organic matter clearly partitioned into one or the other. Actually, we have very little reliable information on the nature of the distribution of particle sizes in seawater. Our usual method for making this determination is the Coulter Counter; we have already discussed the problems involved in making this measurement, both in the taking of the sample and in the measurement procedure itself. This method has the further disadvantage of seeing neither the very large nor the very small particles. It is not likely that we will have any real idea of the particle size distribution in seawater until we can count and measure without actually abstracting the sample from the water. Either optical or acoustical methods would seem to be possible candidates for such measurements.

Once the particulate matter has been filtered, the analyst must decide whether or not to remove carbonate carbon before POC analysis. In certain deep oceanic samples, failure to remove carbonate carbon may result in POC values approximately 30% too high (Iseki, 1981). However, Gordon et al. (1979) noted that in certain surface waters carbonate carbon represents a small percentage of the POC, and thus the carbonate removal step is not necessary. Exposing the filters to dilute HCl solution can cause contamination; fuming with HCl vapor technique is preferred (Gordon et al., 1979).

Two POM sampling methods which have again become popular are in situ pumping systems and moored sediment traps. Both techniques have been in use for a number of years now (Simpson, 1982). Their recent popularity is undoubtedly a result of improved in situ pumping system design (Bishop and Edmond, 1976; Bishop et al., 1980), and a better understanding of the effects of trap design and of current velocity upon trapping efficiency (Gardner, 1980a,b; Spencer, 1981). The advantages and disadvantages of these two sampling methods have been compared by Bishop et al. (1980), Simpson (1982), and by Lee et al. (1983). In many respects the two methods are complementary.

Other interesting observations concerning the sampling of POM should be noted. Bishop and Edmond (1976) observed that the results from their large volume filtration system were similar to those resulting from 30 l Niskin bottle samples. Bates et al. (1983) compared high-speed, continuous flow centrifugation to filtration on Gelman A/E glass fibre filters. They concluded that both methods were similar in terms of size distribution and weight of particulate matter collected. Young and Cline (1983) have demonstrated the use of high speed centrifugation at sea; however, the potential hazards associated with this method when at sea must be kept in mind (Simpson, 1982).

Several factors must be considered when choosing a suitable method for sampling POM. These include sample size required, the environmental time scale of interest, the topography and hydrodynamics of the sampling site, and the actual type of information required. These factors are related in no simple fashion. As a result, the analyst ends up having to choose the method with the fewest problems, as a method having no problems has yet to be invented.

2.3 VOLATILE ORGANIC MATTER

The volatile fraction has recently received attention because of its potential geochemical significance. Unfortunately, the analytical methods for this fraction have progressed little since the mid 1970s. Volatile organic matter (VOM) is still defined by the particular analytical technique used to extract and analyze it. The majority of researchers in this field have chosen the gas stripping technique, thus defining VOM "as those compounds which may be purged from seawater by bubbling with a gas stream and retained by a solid adsorbent" (Gschwend et al., 1980). However, studies reported in the literature indicate that a variety of stripping gases, stripping temperatures, stripping times, and solid adsorbents are being used. This results in a variety of operational definitions for VOM, making intercomparison of studies difficult, if not unwise.

A single basic operational definition is conceivable. Problems arise in finding a procedure which efficiently removes the volatiles from seawater, an adsorbent which efficiently adsorbs and desorbs the volatiles, and an overall procedure which does not contaminate or destroy the volatile compounds.

With few exceptions, recently reported techniques are modifications of the techniques presented by Grob and Zürcher (1976), Bertsch and Anderson (1975), and May et al. (1975). Schwarzenbach et al. (1978) used a modification of the Grob and Zürcher (1976) closed-loop stripping procedure. Headspace air is forced through a glass frit situated near the bottom of the sample container. The effluent air then passes through a charcoal trap which removes the VOM. The compounds are then solvent extracted, and analysed by gas chromatography (GC) or GC/mass spectrometry (GC/MS). The sample water temperature is maintained at 35 °C, and the sample stripped for 2 hr at an air flow rate of 1.5 to 2 l/min. This analytical procedure was also employed by Gschwend et al. (1980) and Gschwend et al. (1982).

Sauer et al. (1978) use a modification of the techniques of Bertsch and Anderson (1975) and May et al. (1975). The procedure is similar to that described above with the exceptions that the water sample is stripped with purified helium gas instead of headspace air, the compounds are trapped on Tenax GC instead of charcoal, and they are desorbed thermally instead of solvent extracted.

Sauer et al. (1978) use a sample water temperature of 70 °C, and strip the sample for 1 hr 40 min at a gas flow rate of 130 ml/min. The compounds are desorbed from the Tenax GC at 250 °C with the helium gas flowing at 40 ml/min for 10 min.

This procedure was later modified (Sauer, 1980). The Tenax GC tube containing the VOM was attached to a six port valve and desorbed for 15 min instead of 10 min. The compounds were then trapped onto a precolumn before injection into the GC. The precolumn eliminated the problem caused by compounds desorbing from the Tenax GC at different times. Having developed the technique for volatile hydrocarbons, Sauer (1981) then applied it to volatile organic matter in open ocean and coastal surface waters. Similar methods have been applied for the measurement of dimethyl sulfide and dimethyl sulfoxide in seawater (Andreae, 1980; Andreae and Bernard, 1983).

MacKinnon (1979) used purified nitrogen gas to strip the volatiles, and Tenax GC as the adsorbent. However, his stripping procedure was radically different from those described above. MacKinnon (1979) first extracted for 4-6 hr with a sample water temperature of 70-80 °C, and a nitrogen gas flowrate of 40 ml/min. A quartz wool trap at -78 °C was also placed in series after the Tenax trap. The sample was then stripped for another 5-7 hr using another Tenax trap and a flowrate of 20 ml/min. The trap was again replaced and stripping continued for another 10-12 hr. The volatile organic carbon included that removed from the three Tenax columns plus the quartz wool trap.

Geodekyan et al. (1979) have reported a method for sampling and analyzing volatile hydrocarbons which is markedly different. They collect the sample using an air tight, specifically designed piston sampler. After collection, the sample is vacuum degassed in a specially designed apparatus, and analyzed by GC-FID. The entire operation is carried out on board ship.

Renberg (1978) determined volatile hydrocarbons in water by passing the sample through XAD-4 resin. Problems such as resin bleed and adsorption of nonvolatile compounds could be encountered when using this method (see discussions concerning XAD resins in sections on hydrocarbons and humic substances). It is also important to note that this method involves an entirely different operational definition of VOM.

Some advances have been made in the sampling of VOM; Schwarzenbach et al. (1978) noted that using lab or ship air for the sample container headspace can cause contamination. As ship air is almost certain to be contaminated with VOM, sampling upwind of the ship is necessary, preferably in a small boat some distance away (Sauer et al., 1978). Sauer et al. (1978) also noted that conventional oceanographic samplers were unsuitable for sampling VOM, and that stripping the sample in the same glass container used to collect the sample reduces the possibility of contamination and loss. Unfortunately, such glass containers are restricted to surface waters due to pressure limitations.

Both charcoal and Tenax GC are excellent adsorbents for hydrocarbons, but have low efficiencies for low molecular weight alcohols and aldehydes. Since the VOM is operationally defined, it is difficult to determine whether one packing material is more suitable for VOM analyses than another. An advantage of Tenax GC is that the VOM are thermally desorbed, and thus the very low molecular weight VOM are not masked by the solvent peak which occurs when the VOM are solvent extracted. However, Tenax GC can bleed contaminants when heated, and it cannot be stored for long periods of time without being recleaned (Sauer et al., 1978). Charcoal, on the other hand, is known to adsorb only some of the possible organics present, and to desorb only some 80% of the material originally adsorbed. The possibility of charcoal-catalyzed decomposition is always present, so one is never certain that what comes off the column is what originally went on.

The overall efficiency of these methods depends not only on the adsorbent, but also upon the stripping method. Kuo et al. (1977) concluded that gas stripping was an inefficient method for removing carboxylic acids and low molecular weight alcohols and aldehydes. Stripping efficiency can be improved by increasing the stripping temperature, but this increases the possibility of thermal degradation of organic compounds. The presence of inorganic salts also affects the stripping efficiency (Kuo et al., 1977; Friant and Suffet, 1979); thus compound efficiencies determined in seawater should be greater than those determined in fresh water.

Although MacKinnon (1979) concluded that the volatile organic carbon represented 1.5 to 6% of the total organic carbon in sea water, other recent studies indicate a VOM fraction representing less than 0.1% of the TOC (Schwarzenbach et al., 1978; Gschwend et al., 1980; Gschwend et al., 1982). This discrepancy may be an indication of the disadvantage of using different operational definitions.

If the only aim of a VOM sampling program is to identify the compounds present, the procedures now available may be sufficient. However, if the aim is to determine the role of VOM in the cycling of organic matter in the environment, then quantification and a knowledge of the flux of VOM is required. Obtaining such information will require fundamental improvements in our analytical methods.

2.4 HUMIC SUBSTANCES

Despite extensive research, we are still able to characterize only a small percentage of the organic matter present in the aquatic environment. The majority of the poorly defined material is believed to have a complex chemical structure and to be resistant but not immune to degradation. Such material has been referred to as humic substances, gelbstoff, and residual organic matter (Kalle, 1966; Ogura, 1977; Bada and Lee, 1977). Interest in humic substances began with soil and freshwater scientists; thus, the majority of the techniques employed for marine humics have been adopted from these fields. This is reflected by the frequent reference in this section to studies of soil and freshwater samples.

Humic substances have a demonstrated role in interactions of such environmental pollutants as trace metals, PCBs, hydrocarbons, and pesticides. They also play a role in the formation of trihalomethanes in drinking water. These processes, along with the overall role of humic substances in the cycling of organic matter in the marine environment, have in recent years spawned a rapidly expanding interest in aquatic humic substances.

Recent applications of established analytical techniques, such as nuclear magnetic resonance, have demonstrated that there are fundamental differences between soil, freshwater, and marine humics. This realization of fundamental differences may lead to the idea that the marine counterparts should not be referred to as humics, thus restricting the application of the term.

However, it is unlikely that such a restriction could easily be accepted; humic substances are at present defined by operation, not environment.

EXTRACTION AND PURIFICATION

Humic substances are defined by the method employed to extract and purify them. The original operational definitions state that humic and fulvic acids are the base extract of soils. The humic acids precipitate in acidic solution, whereas fulvic acids are soluble in both acid and base. Since this original definition, aquatic humic substances have been extracted using such techniques as adsorption, solvent extraction, ultrafiltration, freeze-drying, and precipitation (Thurman and Malcolm, 1981).

Modern procedures for aquatic humic substances employ adsorbent resins and other LC column materials for extraction and purification. Although the resulting product is still referred to as humic substances, it is important to note that this involves a change in the operational definition. This should be considered when attempting to compare data collected by different techniques; each technique will undoubtedly result in a different product. Such a difference resulting from a change in operational definition has been demonstrated for carbohydrates (Thurman and Malcolm, 1983).

Employing adsorbent resins has advantages in that large volumes of water can be processed in short periods of time, expensive organic solvents are not required, recovery efficiencies are high, and interfering organic and inorganic materials are removed (Thurman and Malcolm, 1981). Ultrafiltration offers some of the same advantages; however, it is relatively slow when the humics must be concentrated from large volumes of water, and it makes its separation on the basis of molecular weight rather than of functional groups. Thus, the material separated by ultrafiltration need have no relationship to the original definition of humic and fulvic acids. A major disadvantage of most resins is that they require extensive cleaning procedures before use, and can bleed contaminants if not stored and used in the specified manner (Mantoura and Riley, 1975; Stuermer and Harvey, 1977; Thurman et al., 1978; Aiken et al., 1979; Thurman and Malcolm, 1981). The entire process of resin cleaning, humic extraction, and purification can be monitored by DOC analysis (Thurman and Malcolm, 1981). In fact, DOC analysis has been employed to determine the concentration of humic acids in natural water samples (Fox, 1983).

Earlier studies in the resin extraction of aquatic humic substances generally used XAD-2 (for examples see references in Thurman et al., 1978). This is still a popular resin among marine scientists (Stuermer and Harvey, 1977, 1978; Gillam and Riley, 1982; Fu and Pocklington, 1983; Harvey et al., 1983). However, freshwater and soil scientists have in recent years favored XAD-8 (Aiken et al., 1979; MacCarthy et al., 1979; Leenheer, 1981; Thurman and Malcolm, 1981; Thurman and Malcolm, 1983). This preference for an acrylic ester polymer of intermediate polarity (XAD-8) over a hydrophobic styrene divinylbenzene copolymer (XAD-2) is explained by Aiken et al. (1979), who compared XAD-1, XAD-2, XAD-4, XAD-7, and XAD-8 for concentrating fulvic acids from aqueous solution. They concluded that the styrene divinylbenzene resins (XAD-1, XAD-2, XAD-4) exhibited relatively slow adsorption. They also exhibited inefficient desorption due to charge transfer complexation. XAD-8 was preferred over XAD-7, as the latter exhibited excessive bleeding when the fulvics were eluted with NaOH. This complements a study by Thurman et al. (1978), who used twenty organic solutes to investigate the effects of solute carbon skeleton and functional groups upon XAD-8 retention. Their finding of an inverse correlation between aqueous solubility and retention confirmed that the XAD-8 adsorption process is via hydrophobic effects. This allows estimation of optimal sample for a given column size, and suggests more efficient adsorption from seawater than from freshwater.

A common observation when employing XAD resin to concentrate humic substances is an effect of pH upon adsorption and desorption efficiency. This observation has been investigated by Pietrzyk et al. (1978). Their results indicate that humic type acids would exhibit greater retention when their functional groups are in the neutral form (ie. undissociated), which occurs at low pH; thus the recommendation by Mantoura and Riley (1975) and Thurman et al. (1978) to adsorb at a pH of approximately 2.0. This relationship of adsorption to pH can be used to further advantage as it allows fractionation of the humic substances according to their carboxylic and phenolic functionality (MacCarthy et al., 1979); however, it makes efficient adsorption from seawater dependent upon some form of pH control by acidification before concentration, not always a simple procedure when in situ adsorption columns are to be employed.

Sodium hydroxide solution is usually used to elute the humics from the resin. Organic solvents are not recommended due to limited solubility of humics in these solvents (Mantoura and Riley, 1975; Aiken et al., 1979). Acceptable recoveries have been obtained using ammonia in aqueous methanol (Mantoura and Riley, 1975) and aqueous NH_4OH followed by ethanol and methylene chloride extraction of the NH_4OH eluent (Stuermer and Harvey, 1977); however, it is important to note that this again marks a change in the operational definition. This must be considered when comparing products of this extraction method to those of the methods discussed previously.

More recently it has been suggested that for many purposes a porous teflon could replace XAD-2 as an adsorbent (Josefson, et al., 1984). While this material is somewhat more selective than the XAD resins, it is far easier to clean. The limited selectivity might also be a help rather than a handicap, particularly when the aim of the experimental work is to isolate and characterize a well-defined fraction of the dissolved organic matter.

CHARACTERIZATION

After the humic acids have been extracted and purified, various approaches are available to characterize the sample (Thurman and Malcolm, 1983). Recent studies have employed such techniques as size (apparent molecular weight) fractionation (Ogura, 1977; Buffle et al., 1978; Kerr and Quinn, 1980; Reuter and Perdue, 1981; Thurman and Malcolm, 1981; Thurman et al., 1982), chemical degradation and gas chromatography (Stuermer and Harvey, 1978; Liao et al., 1982; Thurman and Malcolm, 1983), infrared spectrometry (Stuermer and Harvey, 1978; MacCarthy et al., 1979; Dereppe et al., 1980; Leenheer, 1981), and nuclear magnetic resonance (Stuermer and Payne, 1976; Wilson et al., 1978; Ruggiero et al., 1979; Dereppe et al., 1980; Hatcher et al., 1980a, 1980b, 1980c; Saito and Hayano, 1981; Wershaw et al., 1981; Mikita and Steelink, 1981).

Many of these methods have been used in humic substance studies for some time, and are now employed routinely. However, the application of Fourier transform ^{13}C-nuclear magnetic resonance to structural studies of humic substances is a relatively new approach. It has provided considerable information concerning the structures of various types of humic substances, and has led to realization of fundamental differences between marine and terrestrial humics.

3. THE ANALYSIS OF SPECIFIC CHEMICAL CLASSES AND COMPOUNDS

3.1 HYDROCARBONS

Hydrocarbons are one of the most studied classes of organic compounds found in the marine environment. The term hydrocarbon applies to thousands of organic compounds and encompasses a variety of bonds and configurations. Hydrocarbons found in the marine environment have a wide range of aqueous solubility and chemical reactivity, and may have natural and/or anthropogenic sources.

The diverse nature and multiple sources of this class present an analytical challenge of considerable magnitude. The acceptance of this challenge by countless laboratories and individual scientists has resulted in a proliferation of literature on the subject. Several in depth reviews are now available; thus, the purpose of this presentation will be to provide an overview and to identify relevant publications. The reader is directed to Green (1978) for a review of sampling equipment and sample storage, Petrakis and Weiss (1980), Futoma et al. (1981), and Saliot (1981) for hydrocarbon extraction techniques, Albaiges (1978), Cram and Yang (1980) and Futoma et al. (1981) for analyzing hydrocarbons by gas chromatography, Massin (1978), Vollmers (1979) and Bentz (1980) for remote sensing, Petrakis et al. (1980) for the application of NMR, Malins et al. (1980) and Berthou et al. (1981) for complementing gas chromatography with liquid chromatography, Futoma et al.

(1981) for polycyclic aromatic hydrocarbons, Farrington (1980) for an overview of fossil fuel hydrocarbons in the marine environment, and Saliot (1981) for naturally occurring hydrocarbons.

Although state of the art instrumentation can be very precise, various intercomparison studies indicate that the accuracy of the procedures employed can be questioned (Hilpert et al., 1978; Wise et al., 1980; Awad, 1981; MacLeod et al., 1982). These studies also demonstrate that the analysis of hydrocarbons in the marine environment is not simply a matter of choosing an instrument; it involves a multi-step analytical procedure which may also include sample collection and storage, hydrocarbon extraction and concentration, and preanalysis purification. Insufficient consideration of any part of the procedure can result in serious error.

State of the art methods for analyzing hydrocarbons in the marine environment are in a state of imbalance. Resolving and identifying specific hydrocarbons by capillary gas chromatography/mass spectrometry is in an advanced stage, whereas the analysis of hydrocarbons which are not compatible with gas chromatography, along with methods for obtaining 'real-time' data, are still in a stage of development.

The sampling of seawater for hydrocarbons has been reviewed recently by Green (1978). There is little to add to this review at present except to emphasize that in the upper water column in situ pumping methods, such as those described by Osterroht (1977) and Derenbach et al. (1978), have several advantages over bottle sampling; pumping thus may be the primary approach to hydrocarbon sampling in the near future.

Extraction

As demonstrated by intercomparison experiments (Awad, 1981), different extraction techniques are likely to yield different results. The two main approaches to extracting hydrocarbons from seawater are liquid extraction and adsorption onto a solid stationary phase. Liquid extraction employing a variety of non- and low- polarity solvents has been the most popular technique. The solvent of choice will depend upon which class or classes of hydrocarbons are of interest; but for general purposes the chlorinated solvents, such as chloroform or methylene chloride, are probably superior (Futoma et al., 1981; Saliot, 1981).

The drawbacks to liquid extraction are that it requires considerable sample manipulation before analysis and it may extract certain hydrocarbons inefficiently. After solvent extraction, a rigorous procedure is employed to concentrate the hydrocarbons, remove interfering compounds, and to transfer the hydrocarbons into a solvent compatible with the instrument of analysis. Examples of such analytical schemes are presented by Farrington (1980), Malins et al. (1980), Pancirov et al. (1980), Petrakis et al. (1980), and Saliot (1981). Such preanalysis sample preparations run the risk of significant sample contamination and loss. They are also very time consuming.

An alternative to liquid extraction that is gaining popularity is adsorption onto a solid adsorbent. Various adsorbents including XAD resins, Tenax GC, activated carbon, reverse phase C-18, and polyurethane foam have been employed (Green, 1978;

Futoma et al., 1981). Green (1978) recommends XAD-2, but in our opinion further research on the use of solid adsorbents for extracting organic matter from seawater is required before a decision can be made on the adsorbent of choice. For example, several of the papers referenced in the VOM section of this report found that Tenax GC was very efficient for extracting hydrocarbons. The choice between Tenax GC and XAD may depend upon the method used to remove the hydrocarbons from the adsorbent. Tenax GC has superior bleed characteristics when thermal desorption is employed (Futoma et al., 1981). However, both of these adsorbents have significant limitations (Picer and Picer, 1980; Care et al., 1982) and require extensive cleaning before use.

In our discussion of VOM we also reported that activated carbon has provided acceptable extraction efficiencies for hydrocarbons. Adsorption and extraction with XAD resins may be superior to activated carbon (Van Rossum and Webb, 1978). Extraction efficiencies for organic matter may be improved by using a combination of XAD and carbon (Van Rossum and Webb, 1978; Fu and Pocklington, 1983); however, it is doubtful that this will result in better overall efficiencies than can be attained by just using XAD (Van Rossum and Webb, 1978).

Reversed phase-C18 is the dark horse in this group of solid adsorbents in that it has distinct advantages, yet has not been developed for routine extraction of hydrocarbons from seawater. The RP-C18 packing materials do not bleed contaminants during solvent extraction. They specifically extract low and medium polarity compounds, and thus would exclude polar impurities during the extraction step. RP-C18 is compatible with water; in fact, water is generally used as one of the mobile phases when RP-C18 is employed in high performance liquid chromatography (HPLC). This water compatibility leads to several possible applications of RP-C18 in seawater analysis (see section on HPLC).

Unfortunately, there are still several unanswered questions concerning the routine use of RP-C18 for extracting hydrocarbons from seawater. May (1980) demonstrated that short RP-C18 cartridges were greater than 98% efficient for extracting saturated, single aromatic hydrocarbon aqueous solutions of 25 mls or less. Whitehouse (1983) has demonstrated the use of RP-C18 for extracting small volumes of seawater containing an aromatic hydrocarbon at its saturation concentration. Derenbach et al. (1978) have provided some insight into the performance of RP-C18 when using natural seawater and spiked seawater samples. However, research under naturally occurring conditions consisting of multiple component solutions far below saturation concentrations is required in order to determine hydrocarbon extraction and desorption efficiencies, breakthrough volumes, and the optimum cartridge configuration.

Spectrophotometry

Total extract-spectrophotometric methods involve extracting hydrocarbons into an organic solvent and then analyzing for absorption or emission at a specified wavelength. Such methods were popular in the 1970's because of their potential usefulness in monitoring hydrocarbon distribution and concentration.

However, they have experienced little development and less frequent employment in recent years.

There are fundamental reasons which explain why hydrocarbon determination by simple solvent extraction followed by spectrophotometry is rapidly approaching obsolescence. It was always understood that such measurements were not qualitative; however, the usefulness of the resulting quantitative information was not always clear. A severe limitation on the data obtained by such methods is that various hydrocarbons have significantly different quantum yields at a given wavelength. In addition, the marine environment often contains hydrocarbons of various anthropogenic and natural sources (Farrington, 1980; Saliot, 1981), and petroleum in the marine environment is subject to a variety of weathering mechanisms (Atlas et al., 1981; Patton et al., 1981) which rapidly alter the spectrophotometric characteristics of the oil (Bentz, 1980). Thus, using a specific hydrocarbon or oil to standardize the instrument may result in data which are grossly inaccurate.

Although total extract-spectrophotometric methods are decreasing in popularity, spectrophotometry itself has a definite future. The initial requirement for the total extract method is still present; namely, the need for a rapid and relatively inexpensive method that can quantify hydrocarbon concentration and distribution. Examples of application are the mapping of oil spills, detection of hydrocarbon pollution resulting from marine traffic and offshore exploration and production, and the monitoring of chronic inputs into the coastal environment. At present it is possible that these requirements could be met by techniques such as spectrometric remote sensing (Massin, 1978; Vollmers, 1979; Bentz, 1980), and in situ spectrometers.

For monitoring and mapping large areas of the marine environment, remote sensing methods are rapid, are capable of covering large areas simultaneously, and do not require vast amounts of ship time. In situ fluorimeters would be useful for monitoring specific chronic sources such as refinery, production, and sewage outfalls, where the instrument could be calibrated for a specific known source, thus serving as an alarm for changes from ambient conditions. Infrared spectrometers (IR) have been used routinely for oil fingerprinting (Bentz, 1980); in certain cases they may be considered as a possible alternative to the more elaborate method of source identification by GC/MS.

Gas chromatography and GC/mass spectrometry

Without question the most popular and advanced method for analyzing hydrocarbons extracted from seawater is gas chromatography (GC) and GC coupled to a mass spectrometer and computer data system. The technique has a high level of resolution and sensitivity, is capable of quantifying individual compounds or groups of compounds, and is a useful method for identifying hydrocarbon sources (Albaiges, 1978; Cram and Yang, 1980; Futoma et al., 1981).

Gas chromatography/mass spectrometry is similar to other instrumental techniques in that it has limitations. Gas chromatography is not suitable for compounds of low volatility or compounds that are thermally labile (Malins et al., 1980).

Gas chromatographic methods are generally not compatible with water, and thus require analytical procedures to remove the water before analysis. Modern capillary GC/MS systems are relatively expensive and are not designed for field operation, although with care and with properly designed special laboratory modules, they can be used successfully at sea.

Problems associated with the use of MS detectors may lead to increasing use of GC coupled to Fourier transform infrared spectrometry (FTIR) for the analysis of marine samples. Recent advancements in commercially available FTIR spectrometers and associated data systems will undoubtedly increase the environmental applications of this analytical instrument (Azarraga and Potter, 1981; Griffiths, 1983; Wilkins, 1983; Griffiths et al., 1983).

High performance liquid chromatography

High performance liquid chromatography (HPLC) has recently experienced an explosive period of development in terms of pumping systems, columns, detectors, data systems, and applications (Snyder and Kirkland, 1979). It does not have the resolution or sensitivity of state of the art GC. However, volatility and thermal lability are not obstacles in HPLC; thus it may be employed where GC cannot (Malins et al., 1980; Berthou et al., 1981; Krahn et al., 1982). HPLC detectors such as fluorimeters are selective towards certain compound classes (e.g., aromatic hydrocarbons), making it unnecessary to remove nonfluorescing impurities completely prior to analysis. Present day HPLC systems are also capable of stop-flow scanning of UV, fluorescence, and IR spectrums, thus providing identification by methods other than simple retention times. These detectors are nondestructive, thus allowing further sample characterization if necessary.

If one only considers the analytical instrumentation, state of the art HPLC cannot rival GC for general hydrocarbon analysis. However, if the entire analytical procedure of sampling, sample cleanup, and analysis are considered, the potential value of HPLC increases immensely. This is primarily because unlike GC, LC is compatible with water. This opens novel analytical avenues such as in situ trace enrichment, on line sample cleanup, and real time analysis in the field by pumping and direct backflushing into an HPLC system (Eisenbeiss et al., 1978; Ogan et al., 1979; Saner et al., 1979; Van Vliet et al., 1979; Dunn, 1980; Radke et al., 1980; Apffel et al., 1981; Erni et al., 1981; Puyear et al., 1981; Albaiges and Grimalt, 1982: Ogan and Katz, 1982; Sonnefeld et al., 1982; Little et al., 1983). These methods require further development before they can be employed routinely for the analysis of hydrocarbons in seawater (for example, see discussion of the use of RP-C18 packing materials). The tremendous potential advantages of such methods will undoubtedly result in their development in the very near future.

Supercritical fluid chromatography

Another method with potential for extracting and resolving seawater hydrocarbon samples is supercritical fluid CO_2 chromatography (Ehntholt et al., 1983; Gere, 1983; Shafer and Griffiths, 1983). Unlike the organic solvents employed at present, carbon dioxide is nonhazardous, inexpensive, can be obtained free of contaminants, and has a near-ambient critical temperature. Supercritical fluid chromatography complements GC and HPLC; thus, in certain cases it may become the method of choice (Gere, 1983).

3.2 ORGANO-METALLIC COMPOUNDS

The topic of organo-metallic substances in the marine environment includes both specific compounds and operationally defined substances, involving chelation of a metal by an organic matrix that is often ill defined. Thus, this topic could in part be included in the operationally defined section of this report. This dual definition results in widely differing techniques being available for the analysis of organo-metallic substances. The recent review by Mantoura (1981) outlines properties and problems associated with aquatic organo-metallics; thus it serves as a useful introduction to the analysis of these substances.

Although sufficient concentrations may exist in simulated environments (Hunt, 1983) or freshwater environments (Buffle et al., 1977; Hanck and Dillard, 1977; Ryan and Weber, 1982), concentrations of metals and complexing organics in marine environments are such that preconcentration is usually mandatory. The method employed to concentrate the organo-metallic substances will have significant influence upon the data finally obtained.

The analysis of specific organo-metallic compounds is generally more straightforward than the analysis of metals chelated to a poorly defined organic matrix. Earlier studies have been reviewed by Wangersky and Zika (1978) and more recently by Mantoura (1981). Preconcentration onto a solid adsorbent followed by elution and analysis by atomic absorption spectrometry is still widely employed for both covalently bonded organo-metallic compounds and less stable complexes (Stolzberg and Rosin, 1977;

Sugimura et al., 1978a; Betz, 1979; Fujita and Iwashima, 1981; Kremling et al., 1981; Mills and Quinn, 1981; Hirose et al., 1982; Persson and Irgum, 1982). The complexes may also be concentrated by cold trapping (Braman et al., 1977) and analyzed by other spectrometric methods (Braman et al., 1977; Sugimura et al., 1978b). Atomic absorption spectrometry, which has detection limits in the sub-µg/l to ng/l range, has the required sensitivity for the analysis of the resulting concentrated extract (Braman et al., 1977; Fujita and Iwashima, 1981; Persson and Irgum, 1982). Organo-metallic complexes have also been investigated using solid adsorption followed by high performance liquid chromatography (Kremling et al., 1981; Mills et al., 1982; Mackey, 1983).

The majority of studies of organo-metallic compounds in the marine environment attempt to investigate operationally defined metal-organic associations. In these substances the complexation of the metal to the organic matrix represents an equilibrium speciation that may be severely disturbed by sampling and handling. This makes analysis difficult, and indicates that procedures involving extensive handling and analysis time should be avoided. Many of the studies reported attempt to quantify an overall 'complexation capacity' for a given water sample. This usually involves standard additions of a single metal, often copper. The complexation capacity represents moles of added metal complexed per liter of sample (Mantoura, 1981).

The realization of the dynamic nature of these complexes has led to a preference of modern electrochemical methods over methods involving much greater manipulation and analysis time.

Electrochemical techniques have experienced major improvements and expanding environmental application in recent years (Fleet, 1978; Nürnberg, 1982; Piotrowicz et al., 1982). Although polarography is used by environmental scientists (Hanck and Dillard, 1977; Baker, 1978; Fleet, 1978), the marine scientist is likely to find greater application for modern stripping voltammetric techniques (Clem and Hodgson, 1978; Fleet, 1978; Sugai and Healy, 1978; Mart et al., 1980; Fisher and Fabris, 1982; Nilsen and Lund, 1982; Nürnberg, 1982; Piotrowicz et al., 1982; Sueur et al., 1982; Van Den Berg, 1982a). Stripping voltammetry involves a preconcentration step in which the metal species is electrochemically preconcentrated at the electrode before detection. This ability to preconcentrate during instrumental analysis not only eliminates the need for prior concentration, but also greatly reduces sample manipulation and overall analysis time (Mart et al., 1980; Piotrowicz et al., 1982; Nurnberg, 1982). However, only a limited number of trace metals are amenable to this type of analysis.

Because the naturally occurring speciation may be disturbed by sampling, extensive handling, and storage (Mantoura, 1981; Nurnberg, 1982; Piotrowicz et al., 1982; Van Den Berg, 1982b), in situ analysis would obviously be the ideal procedure. At present, shipboard electrochemical analysis immediately after sampling is as close as we have come to this ideal (Mart et al., 1980; Piotrowicz et al., 1982).

Modern differential pulse polarography (DPP) using a dropping mercury electrode (DME) can attain detection limits in the 10^{-7}

M range (Mart et al., 1980). However, modern differential pulse stripping voltammetry (DPSV) can attain several hundred fold concentrations within minutes, resulting in detection limits in the ng/l and sub ng/l range (Mart et al., 1980; Nürnberg, 1982; Piotrowicz et al., 1982). The use of a hanging mercury drop electrode (HMDE) and DPSV can result in detection limits for Cd of approximately 50 ng/l. A rotating mercury film electrode (MFE) and DPSV can go as low as approximately 0.5 ng/l Cd (Mart et al., 1980). Another advantage of the MFE is that it is relatively insensitive to sea motion and ship engine vibration (Nürnberg, 1982). However, MFE may become overloaded at levels greater than several hundred µg/l, thus warranting the use of the HMDE at such concentrations. At concentrations between 0.1 and 500 µg/l, the two electrodes may be equally suitable (Mart et al., 1980). Although in theory the detection limit of DPSV is determined by the cathodic deposition time (preconcentration step), in practice it is generally limited by contamination resulting from sample collection and manipulation (Mart et al., 1980; Van Den Berg, 1982a).

In summary, analytical procedures which alter natural speciation during sampling and analysis may result in an inaccurate interpretation of existing natural processes. The desired procedure must not only be contamination-free and sensitive to the extremely low concentrations encountered in the marine environment, it must also have little influence or an accountable influence upon speciation. Although the application of modern stripping voltammetry to seawater samples can be subject to error (Lazar et al., 1981; Siebert and Hume, 1981), can only be applied to a few of the trace metals of interest, and may be operating at or near its level of detection in some marine environments, at present, it is likely that DPSV with MFE can meet the specified requirements.

3.3 CARBOHYDRATES

The analysis of carbohydrates in seawater has been reviewed by Wangersky and Zika (1978), and more recently by Dawson and Liebezeit (1981). With the exception of a few modifications which are discussed herein, these two reports include the analytical procedures that are employed at present.

The recommended (Wangersky and Zika, 1978; Dawson and Liebezeit, 1981) procedures for total carbohydrates in seawater are those of Johnson and Sieburth (1977) and Burney and Sieburth (1977). This spectrophotometric method had been criticized for its numerous procedural steps and lengthy time requirements. This criticism was met by Johnson et al. (1981), who described a procedural modification that resulted in improved precision and a doubling of the number of samples analyzed in a given time.

Several other spectrophotometric methods are available (see discussion in Wangersky and Zika, 1978). Eberlein and Hammer (1980) have modified the sulphuric acid, L-tryptophane method for total carbohydrates in seawater by using an automated continuous flow system.

Detailed analysis of individual sugars may increase our understanding of the sources and cycling of these compounds in the marine environment. Methods presently employed for this purpose involve some form of chromatography, generally gas chromatography or liquid chromatography. For a review of the analysis of individual carbohydrates using chromatography, the reader is again directed to Dawson and Liebezeit (1981).

The possibility of very high resolution with gas chromatography may be a disadvantage in carbohydrate analysis, as GC has the ability to resolve the anomers of a given sugar. In some cases this may be undesirable, resulting in an unnecessarily complex chromatogram. This can be avoided by the conversion of the sugars to alditols by reduction with sodium borohydride, followed by acetylation (Klok, et al., 1981). High performance liquid chromatography has considerable potential in this area. However, development of suitable detectors is required in order to apply the technique to low concentrations of carbohydrates in seawater. In this respect, the application of electrochemical detectors may prove to be fruitful (Buchberger et al., 1983). Another possibility is the production of fluorescent derivatives of the sugars with 5-dimethylaminonaphthalene-1-sulfonylhydrazine, followed by on-line cleanup and detection by fluorescence (Mopper and Johnson, 1983).

Analysis of specific monosaccharides in samples of natural seawater was reported by Mopper et al. (1980). After desalting by electrodialysis, concentrated extracts were analyzed by two chromatographic techniques, thus improving compound identification by comparing relative retention times. The two anion-exchange resin methods employed were partition chromatography in ethanol (Mopper, 1978a) and separation in borate medium (Mopper, 1978b). The use of such anion-exchange resin techniques for the analysis of carbohydrates has been discussed by Mopper (1978b) and Dawson and Liebezeit (1981).

The analysis of uronic acids, which often make up a considerable portion of the high molecular weight polysaccharides, has also been reported by Mopper and Larsson (1978). They used acid hydrolysis, thin-layer chromatography, and GC/MS for the determination, finding compounds characteristic of marine algae, rather than of terrestrial plants, in the relatively enclosed waters of the Baltic and Black Seas.

3.4 BIOGENIC LIPIDS

When the term lipid is used in oceanography, the term biogenic is often tacitly implied. In addition, the term lipid is sometimes meant to include only those compounds bearing carbonyl and/or hydroxyl groups. These compounds can be grouped into the following classes, in an approximate order of increasing polarity: wax esters, sterol esters, aliphatic ketones, aldehydes, diacyl glyceryl ethers, triglycerides, free fatty acids, free fatty alcohols, free sterols, diglycerides, monoglycerides, glycolipids, and phospholipids. These classes alone include compounds with a wide range of structures and a variety of biological sources, functions, and fates. Technically, however, the term lipid includes all compounds which can be extracted into low-polarity organic solvents. Thus, hydrocarbons, phthalate esters (Ehrhardt and Derenbach, 1980), phenols, pigments, aromatic ketones (Ehrhardt et al., 1982), and even amino acids (Lee and Cronin, 1982) can all be considered to be lipids. These compound types are all potential interferences in the measurement of biogenic lipids.

Total lipid concentrations of 60 to 160 µg/l have been measured in coastal waters for dissolved lipids (Kennicutt and Jeffrey, 1981a) and 9 to 70 µg/l for particulate lipids (Kennicutt and Jeffrey, 1981b). The majority of the compounds present were those whose polarity was close to or greater than that of triglycerides.

Gas chromatography

Gas chromatography (GC) has been the usual means of measuring the components, or the hydrolysis products, of seawater lipid classes. The widely used GC techniques for fatty acids and sterols, and the extraction and sample work-up procedures that accompany them are reviewed in detail by Wangersky and Zika (1978) and by Dawson and Liebezeit (1981). Wangersky and Zika (1978) also noted GC techniques for aldehydes and ketones. Procedures applicable to biogenic hydrocarbons are detailed by Saliot (1981) and in section (3.1) of this text. In addition, sampling and sample work-up procedures for hydrocarbons and phthalate esters (sections 3.1 and 3.5) are also applicable to biogenic lipids.

Some recent examples where GC has been used for marine lipid anlyses include: the analysis of lipids in sea foam (Velimirov, 1982), in suspended and dissolved matter (Kattner et al., 1983a and b), and in sediment trap material (De Baar et al., 1983).

Despite the long history of GC in marine organic chemistry, comparisons between data in the oceanographic literature can be difficult. This is a result of the use of different sampling techniques, and of different approaches to filtration, extraction, and sample clean-up. Some form of reference value is needed for these data. POC and DOC measurements (sections 2.1 and 2.2) can partly fulfill this role. A better approach, however, would be to have some universally accepted reference techniques for the measurement of lipids. These should include standardized sampling and filtration procedures and methods for the analysis of total lipid classes.

Although GC has provided a large body of information on marine lipids, this information is restricted to compounds that are themselves relatively volatile, or else to compounds that become volatile through derivatization. With the use of modern chromatographic technology, efforts are now being made to obtain supplementary information on intact biogenic lipids.

High-temperature glass capillary GC and GC/MS can be used to analyze intact marine fatty acid esters (Wakeham and Frew, 1982). These techniques have been used in the measurement of wax esters, sterol esters, triglycerides and diacyl glyceryl ethers in sediment trap material (Wakeham, 1982). Most of the more polar lipids are not amenable to GC or GC/MS analyses (Kennicutt and Jeffrey, 1981a and b). These lipids can be hydrolyzed and derivatized so that fatty acid moieties can be measured, or else they can be analyzed intact using other chromatographic techniques.

High performance liquid chromatography

High performance liquid chromatography (HPLC) has seen very little use in the analysis of marine biogenic lipids. This is a result of the lack of sensitive detectors for most lipid compounds. UV and fluorescence detectors are only suitable for the direct analysis of a few lipid compounds, or their derivatives (Aitzetmuller, 1982). Short-wavelength UV absorption has been used for the direct analysis of marine lipid classes (Fricke and Oehlenschlager, 1982). However, this approach to lipid detection has serious drawbacks: the choice of solvents is very limited, and lipid class quantification is difficult (Aitzetmuller, 1982). Phenacyl or naphthacyl derivatives of fatty acids permit quantification of as little as 10 ng of these lipid hydrolysis products (Wood and Lee, 1983). Fatty acids from river water samples have been measured in this manner (Hullett and Eisenreich, 1979). Low molecular weight fatty acids have been determined in a similar fashion by Barcelona, et al. (1980). The similarity of these analyses to GC analyses suggests that it is only in specific cases that there would be any distinct advantage in using HPLC for fatty acids. This would not be the case if some form of on-line derivatization procedure could be designed. Oxalic acid and a-keto acids can also be measured by the production of fluorescent quinoxilinol derivatives which can be separated by HPLC techniques (Steinberg and Bada, 1982; Kieber and Mopper, 1983).

Advances in mass spectrometry (MS) technology (Cooks et al., 1983) indicate that sensitive universal detection will soon become possible for HPLC. Sugnaux and Djerassi (1982) discuss the advantages and disadvantages of both on-line and off-line HPLC/MS analyses of marine polar lipids. On-line MS detection is still in the developing stages and it will be several years before HPLC/MS becomes universally available. When this happens a rapid expansion in the field of marine biogenic lipids can be anticipated.

Thin-layer chromatography

There have been few attempts at quantitative analyses of seawater lipids using thin-layer chromatography (TLC). This is surprising considering the excellent lipid class separations that can be obtained on silica layers, and considering that direct quantification procedures have been available for several years. Although quantitative TLC is not as precise and accurate as GC or HPLC, the precision is likely to be more than adequate for many studies. In addition, there are no other techniques currently available which can compare with TLC for the number of lipid classes that can be measured, the number of samples that can be processed, or for the simplicity and price of equipment required.

Ratios of lipid classes have been measured in dissolved matter using densitometry (Kattner et al., 1983b) and in diatoms using flame ionisation detection (Morris et al., 1983). With careful calibration, and with the use of an internal standard (Parrish and Ackman, 1983a), it should be possible to obtain direct estimates of seawater lipid class concentrations. Recent studies on lipid class quantification include those by Banks (1983) and Parrish and Ackman (1983b).

3.5 PHTHALIC ACID ESTERS

Large quantities of *o*-phthalic acid esters (PAE) are used in the plastics industry. These pollutants have been detected in the marine environment in extracts of water, sediments, air and biota. In samples of seawater and sediment, PAE have been detected at higher levels than DDT or PCB (Giam et al., 1978; Murray et al., 1981). Away from direct sources of pollution, seawater concentrations of individual PAE have been reported in the range 0 (with a detection limit of about 0.1 ng/l) to 200 ng/l (Giam et al., 1978; Ehrhardt and Derenbach, 1980; Waldock, 1983). Concentrations in the µg/l range have been detected nearer sources of pollution (Murray et al., 1981; Taylor et al., 1981).

The typical methodology used for PAE determinations consists of extraction with organic solvents or solid adsorbants, separation from other hydrophobic compounds by thin-layer or column chromatography, and analysis by gas chromatography with either electron capture detection, or mass spectrometer ion detection (Giam et al., 1978; Ehrhardt and Derenbach, 1980; Taylor et al., 1981; Waldock, 1983). Single- or multiple-ion detection is extremely sensitive, with detection limits of the order of 10 pg.

Contamination during sample work-up can be a large problem in PAE determinations. It is possible to reduce the risk of obtaining imprecise and inaccurate PAE values by sampling large volumes of water (e.g. by using solid adsorbants and an automatic sampling buoy: Ehrhardt and Derenbach, 1980), and by exercising extreme care in sample handling.

A general description of extraction and concentration techniques for PAE and other hydrophobic environmental pollutants is given by Karasek et al. (1981). Considerable care has to be taken not to add PAE to samples from reagents and equipment used in the laboratory (Ishida et al., 1980), nor to lose PAE from samples during storage (Sullivan et al., 1981) or during sample concentration (Bowers et al., 1981; Karasek et al., 1981).

3.6 PIGMENTS

Phytoplankton chlorophylls have been measured for many years in order to obtain an estimate of phytoplankton biomass or activity. The methods currently in use for the routine determination of pigments are: *in vitro* spectrophotometry and fluorimetry on acetone extracts for chlorophylls *a*, *b*, and *c* and "phaeopigments", and *in vivo* fluorimetric methods for chlorophyll *a*. A detailed evaluation of these techniques has been performed by Lorenzen and Jeffrey (1980). The spectrophotometric equations of Jeffrey and Humphrey (1975) are recommended for quantification of samples from surface waters, and for calibration of *in vivo* and *in vitro* fluorescence methods.

While these spectrophotometric and fluorimetric techniques are well-established, reasonably well standardised, and simple and rapid to use, they are limited in the number of pigments and degradation products that they can measure. They are also limited in their accuracy, selectivity, and sensitivity. Improvements can only be obtained if the pigments in the samples are physically separated from one another before quantification. An accurate measurement of individual pigments within samples greatly extends the usefulness of pigment analyses in seawater.

Thin-layer chromatography (TLC) has been used to separate and identify pigments from coastal and open ocean water samples and from sediment samples (Jeffrey, 1974, 1976, 1981). Cellulose and sucrose adsorption TLC and reversed-phase TLC (Jeffrey, 1974, 1976, 1981; Daley et al., 1973; Scholz and Ballschmiter, 1982) are usually used to separate pigments because artifacts are easily formed on the more reactive silica gel adsorbents. However, good one-dimensional separations are possible on silica gel if precautions are taken against oxidation, and if a long-chain hydrocarbon is added to the developing system (Merzlyak et al., 1983).

Quantification of marine pigments separated by TLC has involved the rather slow and tedious approach of removing the pigment spot from the thin-layer plates and measuring the pigments spectrophotometrically (Jeffrey, 1976, 1981). Chromatograms of pigment separations have been produced by scanning TLC plates with fluorimeters and densitometers (Daley et al., 1973; Merzlyak et al., 1983), and *in situ* quantification of seawater pigments, along the lines used for TLC separations of lipids (Section 3.4), should be considered. However, for more sensitive and precise quantification, high-performance liquid chromatography (HPLC) systems should be used.

The HPLC techniques of Abaychi and Riley (1979) and of Mantoura and Llewellyn (1983) have recently been used to measure pigments in samples from algal cultures, particulate matter, and detritus from the ocean floor (Gieskes and Kraay, 1983; Billett et al., 1983). Shipboard analyses have been performed by Malone et al. (1983), using the HPLC procedure described by Falkowski and Sucher (1981).

There are several methods available for the HPLC separation of various pigments. These include normal-phase (Abaychi and Riley, 1979; Gillan and Johns, 1983) or reversed-phase separations (Falkowski and Sucher, 1981; Goeyens et al., 1982; Scholz and

Ballschmiter, 1982; Mantoura and Llewellyn, 1983). Detection has been by spectrophotometry (Abaychi and Riley, 1979; Scholz and Ballschmiter, 1982; Gillan and Johns, 1983) and by serial spectrophotometry and fluorimetry (Goeyens et al., 1982; Gieskes and Kraay, 1983; Mantoura and Llewellyn, 1983). For most general applications in seawater pigment determinations, reversed-phase separations and fluorescence detection are to be preferred. This is because the usual extracting solvent for marine pigments (90% acetone) can be applied directly to the column, and because fluorescence detection is considerably more sensitive (detection limits are of the order of 100 pg for chloropigments). The addition of an ion-pairing reagent to the mobile phase (Mantoura and Llewellyn, 1983) ensures good reversed-phase resolution of the acidic chloropigments. Reversed-phase cartridges may also be used to reduce the time required for sample preparation (Eskins and Dutton, 1979).

3.7 PHENOLIC COMPOUNDS

Phenolic compounds contain a hydroxyl group attached to a benzene ring or a substituted benzene ring containing one or more of the following: other oxygen containing groups, halogens, alkyl groups, nitrogen containing groups, or other benzene rings. A large number of phenolic compounds may form part or all of a polymeric framework: the term polyphenol has been used to describe high molecular weight polymers exuded by algae (Ragan and Jensen, 1979) as well as lignin and humic substances (Josefsson and Koroleff, 1976). Phenols enter seawater either as part of industrial waste, excretory material, or through the decomposition of polyphenols. Because of the toxic nature of industrially produced phenols there is a considerable literature on analytical methods for their estimation. This literature has been reviewed by Wangersky and Zika (1978), Buikema et al. (1979), and Dawson and Liebezeit (1981). There have, however, been few studies on the occurrence of biogenic and abiogenic phenolic compounds beyond the near-shore region.

Extraction procedures for phenols are reviewed by Dawson and Liebezeit (1981). Phenols may be separated from natural waters by steam distillation, liquid-liquid extraction after acidification, and adsorbtion onto resins. Polyphenols can be extracted from algae by milling the alga in aqueous acetone (Ragan and Jensen, 1977).

The total phenolic content of a seawater extract can be estimated by a variety of colorimetric, spectrophotometric and spectrofluorimetric techniques (Wangersky and Zika, 1978; Buikema et al., 1979; Dawson and Liebezeit, 1981). Variations on the Folin-Denis procedure have been used for the colorimetric determination of "total phenols" in algae (Ragan and Jensen, 1977), and "phenolic reactivity" in the sea surface microlayer and subsurface water (Carlson, 1983). The values obtained by these methods are proportional to the number of oxidizable phenolic hydroxyls present in the sample. It should be noted that aromatic amino groups give an equivalent response (Singleton, 1974).

The direct spectrophotometric or spectrofluorimetric measurement of seawater phenolic compounds is attractive in terms of the simplicity and rapidity of sample handling. The UV absorption of estuarine waters at 280 nm has been found to vary almost linearly with a colorimetric estimate of monophenol equivalents (Carlson and Mayer, 1980). However, a similar experiment with algal polyphenols gave a poor correlation (Ragan and Craigie, 1980). Whether or not a good correlation is obtained with direct spectrophotometric methods, it would be difficult to use this as a quantitative technique because of the likelihood of non-phenolic compounds contributing significantly to the UV absorption of seawater. The aromatic amino acid tryptophane, for instance, also has an absorption maximum at 280 nm (Fruton and Simmonds, 1953). One possible means of alleviating this problem would be to measure the difference in absorption in acidic and basic solutions, provided the pH is not raised to the point where calcium or magnesium precipitate (Wangersky and Zika, 1978).

Modern chromatographic procedures are used for a sensitive quantification of individual phenols in mixtures. Buikema et al. (1979) have discussed GC and GC/MS procedures for a variety of compounds. GC/MS permits the quantitative identification of as little as 10 ng of individual phenols extracted from natural waters and marine sediments (Matsumoto et al., 1977; Matsumoto and Hanya, 1980).

HPLC has not seen much use in the analysis of marine phenolic compounds. A procedure requiring only 5 ml of seawater for the HPLC analysis of pentachlorophenol is described by Giam et al. (1980). This procedure permits the analysis of about 10 samples per hour, but the detection limit is 40 µg/l, and so it is restricted to use with laboratory test systems. A reversed-phase ion-pair system has recently been developed for the determination of nitrophenols (Schultz, 1983). The measurement of the absorption at 405 nm permitted the direct measurement of nitrophenols at a concentration of 10 µg/l in tap water.

Electrochemical detection after HPLC separation shows considerable promise for the analysis of marine phenols. If seawater phenols could be adsorbed onto a resin, desorbed directly into an HPLC system, and finally detected electrochemically, the speed, selectivity and sensitivity of this system would be unrivaled. A new dual-electrode detector has been used to detect phenolic compounds separated by HPLC (Roston and Kissinger, 1982). The electrodes are arranged in series so that oxidative products from the upstream detector are detected by reduction at the downstream detector. This system has shown a linear response between 10 and 700 pmol for several phenolic compounds, and has been used to analyze phenols in a sample of similar complexity to that of seawater (Roston and Kissinger, 1982).

3.8 AMINO ACIDS, PEPTIDES AND PROTEINS

Proteins occupy a central role in the dynamic and structural aspects of life; they are principal components of enzymes, several hormones, and several toxins. A single protein molecule may contain thousands of amino acid units. These units have been found "free" in seawater at concentrations in the nmol/l range with totals in the range 10 to 1000 nmol/l (Garrasi et al., 1979; Bolter and Dawson, 1982; Jorgensen, 1982; Mopper and Lindroth, 1982). Totals for amino acid units in the form of dissolved proteins and peptides have usually been in the µmol/l range (Garrasi et al., 1979; Bolter and Dawson, 1982), while marine particulate protein measurements indicate a concentration range of between 1 and 500 µg/l (Setchell, 1981; Bolter and Dawson, 1982).

Dissolved free amino acids (DFAA)

Of all the primary amine compounds present in seawater it is the DFAA which have received the most attention. The recent advances in analytical techniques for measuring marine amino acids are discussed in detail by Dawson and Liebezeit (1981). The use of fluorimetric reagents has made direct seawater analyses possible, thus eliminating the necessity for sampling large volumes of water. It has also eliminated the use of preconcentration and desalting procedures which are likely to introduce artifacts and contaminants (Garrasi et al., 1979; Dawson and Liebezeit, 1981).

The fluorimetric reagents commonly used are fluorescamine and a phthalaldehyde. Since these compounds react with all primary amines, estimates of total DFAA have to be expressed in relative terms. For instance: o-phthaldialdehyde reactive substances (ORS) have been expressed as µmol glycine/l (Liebezeit et al., 1980).

Using fluorescamine, North (1975) was able to detect as little as 0.2 µmol/l of fluorescamine-positive primary amines in 2 ml of seawater. This technique has been used recently by Amano et al. (1982) in a study involving marine bacteria, and by Laane (1983) to analyze estuarine water samples.

A simple and rapid automated procedure for the analysis of ORS is described by Josefsson et al. (1977). This procedure permits the determination of 20 samples per hour and has a working range of 0.05-15 µmol/l. Modifications to this procedure are described by Dawson and Liebezeit (1981). They found that the response for glycine was linear up to 100 µmol/l.

The next step beyond these total DFAA direct analyses is to insert a chromatographic column either before or after the derivatization step. Separations can be performed with conventional amino acid analyzers, and phthalaldehyde can be pumped into the column effluent prior to detection at the pmol level (Garrasi et al., 1979; Dawson and Libezeit, 1981; Hammer and Eberlein, 1981). Garrasi et al. (1979) were able to inject up to 2 ml of 35 ‰ seawater into such a system; however, the turnover time for a full amino acid analysis was about 4 hours (including column regeneration and re-equilibration). In addition, conventional amino acid analyzers are not particularly seaworthy and so the problems of long-term sample storage (Garrasi et al., 1979; Dawson and Liebezeit, 1981) cannot be avoided. Gradients of temperature, pH, and molarity are used in order to achieve a complete amino acid separation on cation resins (Garrasi et al., 1979; Hammer and Eberlein, 1981). At the expense of obtaining only a partial amino acid analysis, it is possible to reduce the analysis time and to perform the analysis at sea, by using a simplified isocratic analyzer (Garrasi et al., 1979; Dawson an Liebezeit, 1981). However, the ultimate in speed, simplicity and sensitivity can be obtained using precolumn phthalaldehyde derivatization and reversed-phase HPLC separation (Lindroth and Mopper, 1979). This system has a detection limit of about 50 fmol, it separates 25 amino acids, it can measure DFAA in as little as 25 μl of seawater, it has only a 30 minute sample turnover time, and it has been used successfully at sea (Mopper and Lindroth, 1982). This kind of technique will also furnish analyses of compounds such as muramic acid, a metabolite of marine bacteria (Lee, et al., 1983; Mimura and Delmas, 1983).

The HPLC procedure described by Lindroth and Mopper (1979), has been used recently, sometimes with modifications, to measure amino acids in Antarctic, estuarine and Baltic waters (Bolter and Dawson, 1982; Jorgensen, 1982; Mopper and Lindroth, 1982), in sediment trap material (Lee and Cronin, 1982; Lee et al., 1983), and in a study of DFAA uptake by sea urchin larvae (Manahan et al., 1983). This HPLC procedure will undoubtedly see many more applications. It should be noted, however, that there are a few minor difficulties associated with this method (Dawson and Liebezeit, 1981), and that minor modifications are appearing in the oceanographic and chromatographic literature (see literature cited above, and Liebezeit and Dawson, 1981; Jones and Gilligan, 1983; Hodgin et al., 1983; Winspear and Oaks, 1983).

Dissolved and particulate peptides and proteins

The most common approach to the analysis of peptides and proteins in seawater is still the measurement of the component amino acids after hydrolysis (Wangersky and Zika, 1978; Dawson and Libezeit, 1981). Recent examples of this approach include: the analysis of total dissolved amino acids during a plankton bloom (Ittekkot, 1982) using the cation resin method of Garrasi et al. (1979), and the HPLC analysis of phthalaldehyde derivatives of amino acids released from dissolved and particulate matter by HCl (Bolter and Dawson, 1982; Lee and Cronin, 1982; Lee et al., 1983). There are a few problems associated with hydrolysis procedures (Dawson and Liebezeit, 1981), and so some means of quantifying intact proteins and peptides is desirable.

Total particulate protein can be measured by a modification of the Coomassie Brilliant Blue protein assay (Setchell, 1981). This technique is less sensitive than fluorimetric analyses, but it is more specific: the dye binding assay is apparently so specific for proteins that small peptides do not interfere.

HPLC will undoubtedly prove to be one of the better tools for increasing our knowledge concerning peptides and proteins in seawater. Recent advances in HPLC packings designed for the separation of biopolymers (Regnier, 1983a) have lead to exponential growth in biochemical literature concerning HPLC separations of peptides and proteins (Regnier, 1983b). Some of the procedures used for the pmol measurement of proteins and peptides (e.g. Stein and Moschera, 1981) are similar to those we are already using for DFAA analyses. The applicability of HPLC techniques for seawater biopolymer analyses should be investigated.

4. RECOMMENDATIONS

With the recommendation of the automated, shipboard photo-oxidation method for DOC analysis, the CHN analyzer for POC analysis, and shipboard electrochemical methods for organo-metallic complexes, it is evident that the main problems in the analysis of these 'fractions' at present are sampling and definition. Sampling and analysis go hand in hand in oceanography; thus one should not be considered without the other. This report has demonstrated that the procedure used in laboratory analysis of discrete bottle samples may greatly influence the data finally obtained. This is especially true in the study of organo-metallic complexes and particulate organic matter.

Unfortunately, superior alternative methods are few. Greater attention should be given to in situ methods. For the organo-metallic complexes, the possibility of in situ electrochemical analysis should be explored. Moored sediment traps and in situ pumping through filters have increased our understanding of POM in the marine environment. An in situ method allowing an undisturbed continuous view of particle size distribution in time and space is now required.

The filtration of seawater samples for analysis of organic matter will always be open to criticism. It is unlikely that any filter could be developed which would avoid all of the problems that can be encountered. A fundamental difficulty is our concept that everything below a discrete size can be considered "dissolved" and everything above as "particulate". Although this may be an acceptable approximation in some cases, the inaccuracies associated with this concept are becoming increasingly evident. We must not lose sight of the fact that organic matter exists in seawater in a continuous spectrum of sizes and phases.

The analysis of volatile organic matter is in a state of disarray. Here we have an operationally defined fraction with no accepted referee operation. The comparison of data collected by different methods is difficult in such a situation. Scientists working in this field should give greater consideration to intercomparison of their methods.

The past few years have witnessed significant advances in our understanding of humic substances. The application of NMR has played a significant role in this. It is now evident that extraction (and thus definition) by XAD resin is widely accepted. Of interest here is the observation of a divergence between the marine and soil-freshwater scientists. Marine chemists appear to prefer XAD-2 whereas the soil-freshwater chemists are using XAD-8. Marine chemists should give greater consideration to XAD-8, as it appears to have superior adsorption-desorption properties. In addition, XAD-8 has been more extensively characterized as an adsorbent for humic substances.

The analysis of compound classes is similar to that of operational fractions in that the entire process of sampling, handling, and analysis should be considered together. Each step influences the final results. Again, this potential influence may be reduced by the development of in situ techniques such as in situ pumping through filters and solid adsorbents.

A recommendation common to both this report and that by Wangersky and Zika (1978) is further application of high performance liquid chromatography to the analysis of organic compounds in seawater. Considerable potential exists here, but applications to seawater are slow in appearing, largely because of limitations in HPLC detectors. The recent application of HPLC to pigment analysis is encouraging, and demonstrates how our concepts and understanding of organics in seawater can be altered by analytical procedure.

In the past five years, the greatest advances in analytical methodology have come through the application of physical methods and of automated sample handling to marine problems. Some of these techniques require the stabilized environment and steady power supply of the shore laboratory. Many, however, could be adapted to the shipboard laboratory with only minor modifications. Still others could be incorporated into microprocessor-controlled units for true in situ analysis. These are directions in which we must eventually go; the capability already exists, and we see no valid reason for waiting for some more propitious moment in the distant future.

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Committee on Marine Analytical Chemistry

1984

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Terms of Reference for the Committee

To provide a forum for the synthesis of advice to the National Research Council on matters pertaining to marine chemistry, and a mechanism for the coordination of research activities related to the provision of reference materials and analytical problems of marine materials. More specifically:

- to review as necessary, the status of marine chemistry in Canada and particularly the National effort in marine analytical chemistry.

- to coordinate the continuing development of standard reference materials, standard methods and interlaboratory calibrations.

- to anticipate the long term developmental needs and requirements of marine analytical chemistry in the private and public sectors, recommend priorities, and estimate the resources required to meet the needs.

- to promote communication between marine and analytical chemistry groups, assist in the exchange of information, and recommend mechanisms for improving liaison.

- to study specific problems at the request of various agencies concerned with the analysis of marine materials.

Comité de chimie analytique marine

1984

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Mandat du Comité

Son rôle est de constituer un forum qui réunit les diverses opinions sur les sujets se rapportant à la chimie marine et de les transmettre au Conseil national de recherches; de coordonner les activités de recherche en ce qui a trait aux problèmes d'analyse et à la mise au point de nouveaux standards. De façon plus précise:

- vérifier au besoin la situation de la chimie marine au Canada et en particulier l'effort national dans le domaine de la chimie analytique marine.

- coordonner la mise au point constante de standards, de méthodes d'analyse et de systèmes de comparaison entre les laboratoires.

- prévoir les besoins et les exigences à long terme du développement de la chimie analytique marine autant dans le secteur privé que public, établir les priorités et évaluer les ressources nécessaires pour répondre à ces besoins.

- favoriser les échanges entre les groupes qui étudient la mer et la chimie analytique, aider l'échange des renseignements, et proposer des methodes d'améliorer ces échanges.

- étudier des problèmes particuliers à la demande de divers organismes qui s'intéressent à l'analyse d'échantillons marins.