

*Determination of
Organic Substances
in Water*

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Determination of Organic Substances in Water

Volume 1

T. R. CROMPTON

A Wiley-Interscience Publication

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Preface

The presence of concentrations of organic substances in water is a matter of increasing concern to the water industry, environmentalists and the general public alike, from the point of view of possible health hazards presented to both human and animal life represented by domesticated and wild animals, bird and fish life. This awareness hinges on three facts: the increasing interest of the scientist and the public alike in matters environmental, an increased usage of organic materials in commerce coupled with the much wider variety of organic substances used nowadays, and finally, the availability of analytical methods sensitive enough to determine very low concentrations of these substances, the presence of which we were formerly unaware.

It has been estimated that river waters can contain up to two thousand different organic substances over a wide concentration range, many of which survive processing in the water works and occur in potable water with possible health implications. The Food and Drug Administration in America, amongst others, is systematically working its way through screening tests on the substances so far identified in water, but this is a process that will take many years to complete.

As well as organics occurring in water as a direct result of industrial activity there are those which arise more indirectly, such as haloforms produced in the chlorination stage of water treatment process, organio-metallic compounds produced by conversion of inorganic salts by biological activity in rivers and nitrosamine formation by conversion of inorganic nitrites. There are also, of course, naturally occurring organic substances in water.

The purpose of this work is to draw together and systematize the body of information available throughout the world on the occurrence and determination of organics in all types of water and effluents. A particular feature is the presentation of detailed procedures in the case of many of the more important procedures, so that reference to a very scattered literature can in many cases be avoided. Complete coverage is given of all the major instrumental techniques now available.

The contents are presented in as logical a fashion as possible, starting in Volume 1 Chapter 1 with a discussion of hydrocarbons and polyaromatic hydrocarbons. Chapter 2 deals with the various types of surface active agents whilst Chapters 3 and 4 respectively discuss the numerous types of organochlorine and organophosphorus insecticides and herbicides and polychlorinated biphenyls now

in use in agriculture and which are finding their way into the water courses. Volume 2 deals with organometallic compounds, types of compounds classified under elements including carbon, oxygen, halogen, nitrogen, sulphur and phosphorus and concludes with chapters on ozonization products and natural pigments.

Particular groups of substances which are causing concern by their presence in the environment are discussed in detail, e.g. polyaromatic hydrocarbons, chlorine and phosphorus insecticides, herbicides, polychlorinated biphenyls, haloforms and organometallic compounds.

As well as discussing the analysis of river, surface and underground waters and potable water, various sections include discussion, where relevant, of ocean and beach waters, sewage and trade effluents and muds and sediments. In certain instances, the analysis of fish, crustaceae and plant life for organic pollutants is also discussed. Such measurements are very useful as these will reflect the general level of pollution that has occurred over a period of time, as opposed to spot measurements obtained by analysis of water samples.

Examination for organic substances combines all the exciting features of analytical chemistry. First, the analysis must be successful; and in cases such as spillages must be completed quickly. Often the nature of the substances to be investigated is unknown; they might occur at exceedingly low concentrations and might indeed be a complex mixture. To be successful in such an area requires analytical skills of a high order and the availability of sophisticated instrumentation.

The work has been written with the interests of the following groups of people in mind: management and scientists in all aspects of the water industry, river management, fishery industries, sewage effluent treatment and disposal, land drainage and water supply; also management and scientists in all branches of industry which produce aqueous effluents. It will also be of interest to agricultural chemists, agriculturalists concerned with the ways in which organic chemicals used in crop or soil treatment permeate the ecosystem; also to the biologists and scientists involved in fish, insect and plant life, and to the medical profession, toxicologists and public health workers and public analysts. Other groups or workers to whom the work will be of interest include oceanographers, environmentalists and, not least, members of the public who are concerned with the protection of our environment.

Finally, it is hoped that the work will act as a spur to students of all subjects mentioned and assist them in the challenge that awaits them in ensuring that the pollution of the environment is controlled so as to ensure that by the turn of the century we are left with a worthwhile environment to protect.

T. R. CROMPTON

Contents

Preface	vii
1. Hydrocarbons	1
Oils and petroleums	1
Aromatics	116
Polyaromatics	129
Greases	200
References	205
2. Detergents	218
Anionic detergents	218
Cationic detergents	247
Non-ionic detergents	249
References	277
3. Pesticides and PCBs	280
Organochlorine insecticides	280
Carbamate insecticides	361
Organophosphorus insecticides	371
PCB and PCB-organochlorine insecticide mixtures	416
References	483
4. Herbicides	495
Introduction	495
Triazine type herbicides	498
Substituted urea type herbicides	503
Phenoxyacetic acid type herbicides	514
Miscellaneous herbicides	529
Mixture of herbicides and organochlorine insecticides	542
References	545
Index	549

Chapter 1

Hydrocarbons

OILS AND PETROLEUMS

In many areas oil has become the most frequently encountered water pollutant, and oil pollution incidents are becoming more numerous. This reflects the expanding and widespread consumption of petroleum products, a consumption that will continue to increase in the foreseeable future. Oil pollution has harmful effects on aquatic life and lowers the aesthetic appearance of an inland water. Occasionally it necessitates the closure of waterworks intakes. Existing legislation concerning oil pollution cannot be effective unless there are adequate analytical means of detecting oil pollutants, identifying them with regard to their sources and determining their concentration. Many analytical techniques have been proposed, but the references are scattered throughout the literature, and require collation and assessment in relation to inland water pollution.

Although marine oil pollution has received much attention in recent years, this has not been the case with oil pollution of inland waters, and for some time now there has been need for an assessment of the analytical and related problems in this field. This chapter discusses these problems. Particular attention is given to the identification of the polluting oil.

Wherever oil is produced, stored, transported by vehicle or pipeline, or consumed, there exists a potential source of oil pollution, either directly by surface drains and surface run-off, or indirectly by seepage into the ground. Unlike some pollutants, oil pollution is generally unpredictable as to location and time, and usually exists as a surface phenomenon. Heavy pollution is obviously unwelcome, but even thin ephemeral films representing only small amounts of oil may cause complaints and require investigation if continually present on surface water.

The effects of oils on water are manifold, and generally only the acute effects are understood. Long-term chronic effects are slightly comprehended, if at all. Oil, directly or indirectly, seriously lowers the aesthetic appearance of inland waters and interferes with their recreational use. Since oil can readily form a visible thin film of about 7.6×10^{-5} mm thickness, a small quantity of oil may be important and produce a heavily polluted appearance.

It is often claimed that oil affects the transfer of oxygen into water, but the significance of the effect in the case of thin films is not fully understood. Thick viscous layers do affect the transfer.

Photosynthetic activity can be affected by increased reflection and possibly by the absorption of light by the oil. On rivers, where a continuous, prolonged oil slick is improbable, the effect would probably not be significant.

Biodegradation of oil in inland waters depletes the oxygen content, but unless frequent oil pollutions occur in a river, such as in heavily industrialized areas, or in non-flowing waters, the depletion would probably do little damage.

Most oil products are not considered particularly toxic. Petrol, white spirit and similar volatile products are generally regarded as the most toxic. Heavy surface oil pollution and oil which is emulsified, dissolved, or associated with suspended solids in the body of the water may injure or kill aquatic animal life. Plant life, both aquatic and riparian, can be destroyed by heavy pollution. Prolonged pollution will denude most plant and animal life by a combination of the above mentioned effects. Long-term toxicity effects are not really understood although carcinogenicity and general health considerations have been studied in some detail.

Recent information suggests that sedimented oils in a lake or river can act as carriers of toxic non-polar organic chemicals, e.g. DDT, owing to the high solvent power of sedimented oils for this type of compound. The significance of this effect in rivers is unknown.

Oil contamination is most undesirable in waterworks treatment systems. High concentrations of oil can impair the filters, while even trace quantities can produce taste and odour problems.

Practically the total range of petroleum products is encountered as pollutants on inland water. Crude oils are very seldom found inland, but petrol, paraffin, gas oils, heating fuels, lubricating oils, transformer oils and cutting fluids have given problems. In most areas, heating fuel, due to its widespread industrial and domestic utilization, and diesel fuel are the most commonly occurring oil pollutants. Petrol, although used in greater quantity than most other petroleum products, does not often pollute inland waters. Probably this is due to its high volatility on water surfaces, the strict regulations concerning its storage, and the general public awareness of its dangers. Its relatively high water solubility may be a lesser factor. Lubricating oils give pollution problems especially in highly industrialized areas. Since lubricating oils are seldom stored or used in large quantities, pollutions tend to be of a smaller nature, but are often responsible for intermittent surface films on inland waters, which are regarded as insignificant. However, the increase in concern over the aesthetic appearance of our inland waters may soon render them significant. Lubricating oils are common pollutants at sewage works. Heavy fuel oils are occasionally met as pollutants, and owing to their high viscosity can cause extensive soiling of banks and riparian structures as well as being extremely difficult and troublesome to remove.

Natural oils, such as essential oils, vegetable, animal, and fish oils, are only

infrequently found as significant pollutants. However, when they do occur they can pose extremely difficult problems.

Characterization/identification

The identification procedure for oils in water samples, whether river or ocean can be divided into three stages:

- (1) isolation of the hydrocarbon components from the pollutant sample.
- (2) identification of the sample in terms of the petroleum product, for example, crude oil, petroleum, gas oil etc.
- (3) identification of the specific source of pollution, such as an individual tanker, tank truck, factory or domestic fuel tank etc.

Stage (2), a general classification of the oil, is often satisfactorily achieved by gas chromatographic techniques possibly coupled with mass spectrometry or infrared spectroscopy applied to a sample of the oil pollutant. Stage (3), the true identification, invariably requires samples from potential sources for comparison with the pollutant. This is often attempted again using gas chromatography, by comparison of the resulting chromatograms, but in a less satisfactory and confident manner. Generally, when the comparisons of chromatograms are reasonably similar, the perpetrator of the pollution accepts liability in the face of accumulated circumstantial and scientific evidence, and introduces the recommended remedial measures.

Existing gas chromatographic techniques can, in the majority of cases, classify petrol, paraffin, light fuel oils, intermediate fuel oils and, with less ease, lubricating, transformer and cutting oils. Higher boiling products with little volatility are not amenable to conventional gas chromatographic techniques and recourse has to be taken to other techniques such as the use of capillary columns or non-g.l.c. techniques.

Techniques other than gas chromatography or, more commonly, combinations of techniques have been used to characterize oil spills, as discussed below.

Nearly every known analytical technique has been used or suggested for oil pollutant identification, but, certainly, no one has emerged of such superiority that all the others can be considered as redundant. Therefore, earlier attempts of oil characterization have been performed by a multimethod approach; the particular combination of analytical techniques depends on the facilities and the experience existing in a laboratory and the expenditure which is justified to identify any unknown source.

Representative examples of these overall approaches are reported in Table 1. They include analytical determinations such as the infrared spectra, asphaltene and paraffin contents, etc., that provide a general classification of the pollutants (crude oils, fuel oils, oil sludges, etc.) and others, such as the Ni/V ratio, sulphur content, chromatographic profiles, etc., that permit, by comparison with reference samples, their precise identification.

Table 1 Overall approaches for identification of oil pollutants

IP Method (1974)	Sp. gr. Asphaltenes S, Ni, and V contents T.l.c./u.v. G.l.c.
DGMK Method (1973)	I.r. spectroscopy S, Ni, and V(Ca, Ba, and Zn) Column chromatography G.l.c.
US Coast Guard (1974)	I.r. spectroscopy Fluorescence spectroscopy T.l.c./u.v. G.l.c.

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Table 2 Multiparametric methods for fingerprinting oil pollutants

Analytical methods	No. of parameters	References
Trace elements	3	Brunnock <i>et al.</i> ¹
	22	Duewer <i>et al.</i> ²
I.r. spectroscopy	3	Kawahara and Ballinger ³
	18	Lynch and Brown ⁴
	23	Mattson <i>et al.</i> ⁵
Gas chromatography	3	Erhardt and Blumer ⁶
	19	Clark and Jurs ⁷
	36	Rasmussen ⁸

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However, another approach involving only one analytical technique, but increasing the number of parameters considered, has been emphasized recently as is exemplified in Table 2 for trace analysis, infrared spectroscopy and gas chromatography. In these cases a multiparametric profile is used for identification, instead of a combination of different analytical determinations and pattern recognition techniques have, often, been applied to improve the diagnostic performance.

The main requirements that must fulfil these fingerprinting parameters besides their specificity, is that they must remain unaltered during the sea weathering processes affecting the pollutant, namely by evaporation, solution, photo-oxidation, and biodegradation. In consequence, both conditions, specificity and stability, need to be investigated in order to evaluate the reliability and the usefulness of any proposed method.

General weathering effects occasionally affect identification, and chemists are conscious of the possibility that weathering action on the polluting oil may

prevent identification or lead to an incorrect inference. In most cases, since an oil would be unlikely to remain on an inland surface water for any length of time prior to analysis, these effects are probably limited to evaporation of the more volatile components, and to a lesser extent, of the more water-soluble components. With practice most analysts can allow for small evaporation effects during the visual inspection of the chromatograms. Little is known of the significance or nature of solution of components on identification. With material of much less volatility than petrol the effect would probably be small.

Quantitative analysis of oils polluting the surface of a river is seldom attempted, as the information is not particularly useful. The pollution is obvious, and the value obtained meaningless, because it is impossible quantitatively to determine oil films or slicks, and relate the determination to the total volume of water, the total film area, and the film thickness.

Quantitative results for oil are, however, required on effluents entering rivers. The method often used is a gravimetric procedure⁹ which determines 'non-volatile ether-extractable matter'. The method is non-specific for petroleum oils, gives erroneous results when soluble oils (cutting oils, etc.) are present, and is inaccurate below 5 mg oil/litre range. Many analysts are dissatisfied with this procedure. Thin-layer chromatography and infrared analysis offer specificity and accuracy in the low concentration range and will be discussed later.

The problems associated with the characterization of oils and the determination of oils are discussed in detail below under separate headings.

In the case of heavy oil pollution, a sufficient sample of the neat oil is readily taken from the surface. Smaller quantities of oil, for example, thin films and emulsions, can be liquid-liquid extracted with carbon tetrachloride,^{10,11} chloroform,¹² pentane,¹¹⁻¹³ ether,^{14,15} nitrobenzene,^{16,17} methanol/benzene (for sediments),^{18,19} hexane,²⁰ toluene/xylene, toluene,²¹ and iso-octane.¹³ Solvents are chosen in order that no significant interference occurs to the components of the pollutant, and that loss of volatile components during evaporation of the solvent, if required, is minimal. For very volatile hydrocarbons in aqueous samples, head-space analysis and degassing techniques are recommended.²²⁻²⁴ Goma and Durand used an ultrasonically prepared emulsion for their gas chromatographic work, thus avoiding quantitative liquid-liquid extractions.²⁵

Most authors recommend collection and storage of samples in glass containers. Plastic containers may introduce organic contaminants which may be significant,¹⁴ especially with trace amounts of oil. Metal containers may affect subsequent determinations of nickel and vanadium in crude in residual petroleum oils.²¹ Pollutants on the surface can be collected by skimming with a suitable container. Kawahara¹² suggests a glass, wide-mouthed filter-funnel fitted with Teflon tubing and a two-way stopcock. The surface oil is ladled into this and is repeatedly separated from the lower aqueous phase. Alternatively, a paint-free dustpan with a stopcock attached to the handle, or even a mop with a fitted wringer, have been employed with success.

Samples can be preserved to a limited extent by the addition of solid carbon dioxide to expel air, by refrigeration,¹² or by the addition of mercuric chloride which inhibits bacterial activity.²⁴

Invariably, dual packed columns have been employed, and one of the earliest articles devoted to the identification of petroleum products is that of Lively,¹³ who used dual 4 ft \times $\frac{1}{4}$ in. columns packed with 20% SE-30 as the liquid phase on a Chromosorb solid support. Most subsequent workers in this field have employed the same or a similar liquid phase, usually at a lower loading of 4–5% and somewhat different column dimensions, 4–12 ft \times $\frac{1}{8}$ – $\frac{1}{4}$ in.^{10–12,16,20,21,26–31} Chromosorb, or occasionally a similar solid support²⁹ was usually the solid support utilized after first being acid washed and treated with hexamethyl disilazane (HMDS) or dimethyl dichlorosilane (DMCS). Liquid phases of similar properties that have been employed are 5%²¹ and 10%³¹ OV-1, 20% SE-52,²⁷ 5% E301,²⁸ and 2.2%,³² 10%,³³ and 20%³⁰ Apiezon L. These liquid phases are essentially non-polar substances, but more polar phases, 5%¹⁷ and 10%¹⁶ polyethylene glycol 1500, have been used for investigations of the water-soluble components in diesel and gas oil¹⁷ and in petrol.¹⁶

In almost all recent publications, flame ionization detectors and temperature programming were employed, the latter especially in the identification of less volatile oils. For routine investigations, isothermal conditions have been adopted in order to allow quicker analysis, but at the sacrifice of some fine detail in the chromatogram.³⁰

Columns containing relatively non-polar liquid phases, separate homologous series of hydrocarbons virtually in order of boiling point. In practice, this results in the *n*-alkanes of petroleum products being separated in order of increasing number of carbon atoms in the molecule. Branched-chain, saturated and aromatic hydrocarbons follow a similar pattern although possibly less precisely. With products such as petrol, paraffin, diesel oil, gas oils, TVO, and intermediate fuel oils, *n*-alkanes produce a predominant series of well separated peaks on the chromatogram, indicative of the boiling range of the sample. The *n*-alkanes on the chromatogram usually reside on a mound of poorly resolved branched and cyclic paraffins, aromatic hydrocarbons, and heterocyclic compounds. In the case of lubricating, cutting and transformer oils, which are generally lacking in *n*-alkanes, only fairly featureless mounds are obtained. Pollutants are classified as to type principally by examination of the carbon number range and proportion of the *n*-alkanes on the chromatogram. Specific *n*-alkane peaks are usually identified by comparison with standard solutions of some known compounds and a 1% w/v solution has been recommended.¹¹ Identification of the source of pollution is achieved by comparison of pollutant and suspect oil chromatograms, usually by matching minor component peaks. It has been stated that while *n*-paraffins tend to be indicative of the processing of a product, the minor components are more specific and can indicate the original crude oil source. With gas chromatography small evaporation effects can be allowed for by expecting irregularities in the volatile component peaks.

Detailed salient points involved in classifying and identifying oils have

been compiled.^{11,21,27,28,34,35} Most distillate products e.g. petrol, paraffin, fuel oils, diesel oil, TVO etc., and even very similar products such as turbo-jet fuel and kerosene,²⁷ can be classified in the absence of excessive weathering effects. Various chromatograms have been published: kerosene, turbo-jet fuel, steam-cracked naphtha;²⁷ lubricating oil/gas oil/weathered paraffin;³⁵ white spirit, turpentine substitute, paraffin, 30 second fuel oil;³⁰ standard gasoline;¹³ petrol;¹⁶ diesel fuel and gas oil,¹⁷ various gasolines, diesel fuels, and aviation fuels.³³

Lubricating, cutting, transformer oils etc., heavy fuel oils, asphaltic and bituminous materials are difficult or impossible to classify with any certainty by gas chromatography.

Characterization of hydrocarbons in river water

A polar liquid phase was found more suitable for studying the major components of petrol,¹⁶ gas oil, and diesel oil,¹⁷ forming true solutions in water. With such a phase, saturated hydrocarbons tended to elute before aromatic hydrocarbons which were found to be the principal components in true solution, and therefore their investigation was facilitated, in the case of gas oil and diesel oil, forming true solutions in water. With such a phase, saturated hydrocarbons tended to elute before aromatic hydrocarbons which were found to be the principal components in true solution, and therefore their investigation was facilitated. In the case of gas oil and diesel oil, no saturated hydrocarbons could be detected in solution. These authors reached the important conclusion that the determination of the origin of oil components in true aqueous solution could be more difficult because of selective solution of certain components. This effect was likely to apply to the lower distillates, which tended to be relatively more water soluble, rather than to the non-volatile petroleum products. Distinction between petrol and gas oil or diesel oil seemed possible, but appeared difficult between similar products such as gas oil and diesel oil.

Capillary columns provide greater resolution and therefore more detail for comparison between a polluting oil and a suspect sample. The enormous separation power available has been demonstrated in their application to petroleum analysis. Sanders and Maynard,³⁷ using a 200 ft \times 0.01 in. column containing squalane, separated approximately 240 hydrocarbon components of gasoline, of which 180 were identified. Gouw³⁸ describes a versatile 10 m \times 0.01 in. capillary column coated with CV-101, and its application to the separation of hydrocarbon mixtures in the C_4 - C_{38} *n*-alkane range. Columns of 500 ft \times 0.01 in. coated with 1-octadecene and operated at 30 °C have been recommended for identification of crude oils.¹² Hydrocarbons of a selected boiling range, e.g. C_7 - C_8 saturates, were collected by prefractionation in a short packed column, trapped, and finally examined on the capillary column. Alkylbenzenes up to C_{10} were examined in a similar manner on a 800 ft \times 0.01 in. column coated with more polar polyethylene glycol and operated at 60 °C. It is claimed that gasoline and other volatile products can be analysed

and identified. However, the technique in no way allows for evaporation of volatile components, which would have a serious effect. Columns of the stated length would be impractical for general routine use.

Cole³⁹ found that in the identification of kerosene and aviation fuels, the usual packed columns provided sufficient detail only up to C_{13} *n*-alkane, a range readily altered by evaporation effects. A suitable capillary column was developed which revealed extra detail of minor components above C_{13} *n*-alkane, and consisted of a $45\text{ m} \times 0.25\text{ mm}$ stainless steel column coated with OV-101. This gave satisfactory resolution and stability in the $50\text{--}310^\circ\text{C}$ temperature range. Naturally abundant saturated terpenoid substances, e.g. farnesane (C_{15}), pristane (C_{19}) and phytane (C_{20}) were determined in fractionated crude oils and used for identification purposes. The use of a similar column should be applicable to general identification of the commonly occurring oil pollutants of inland waters up to the $C_{25}\text{--}C_{30}$ *n*-alkane range. This seems a logical and valuable extension of the present gas chromatographic techniques. Unfortunately the application to analysis of lubricating oils, etc., does not seem promising. The cost and stability of such a capillary column seems satisfactory for routine uses.

An interesting gas chromatographic technique of identifying petroleum products, including lubricating oils, is that of Dewitt Johnson and Fuller.³¹ A gas chromatographic column effluent was split in order that it could be simultaneously sensed by a double-headed flame photometric detector, specific for both sulphur and phosphorus compounds, and by dual-flame ionization detectors for carbon compounds in general. Since most petroleum products are claimed to contain sulphur and phosphorus compounds, three chromatographic traces were obtained for the products examined. In the cases of lubricating oils, which normally give poorly resolved peaks on chromatograms with flame ionization detection, sulphur and phosphorus detection gave considerably more detail for identifying purposes. The apparatus is, however, complex and expensive for routine application.

Lysyj and Newton⁴⁰ have described a multicomponent pattern recognition and differentiation method for the analysis of oils in natural waters. The method is based on that described earlier by Lysyj⁴¹ which depends on the thermal fragmentation of organic molecules followed by gas chromatography. Dried algae and outboard-motor oil were analysed and a specific pattern or numerical 'fingerprint' was obtained for each by pyrographic means. The algal pattern comprised three specific peaks and seven peaks common to those of the oil, whereas the oil pattern comprised two specific peaks and seven peaks common to those of the algae.

Kawahara⁴² has discussed the characterization and identification of spilled residual fuel oils on surface water using gas chromatography and infrared spectrophotometry. The oily material was collected by surface skimming and extraction with dichloromethane, and the extract was evaporated. Preliminary distinction between samples was made by dissolving portions of the residue in hexane or chloroform. If the residue was soluble in chloroform but not in hexane

it was assumed to be a crude oil, a grease, a heavy residual fuel oil or an asphalt; if it was soluble in both solvents it was assumed to be a light or heavy naphtha, kerosene, gas oil, white oil, diesel oil, jet fuel, cutting oil, motor oil or cutter stock. The residue was also examined by infrared spectrophotometry; wavenumber values of use for identification purposes are tabulated. Classified, volatile petroleum products such as naphtha, gasoline, jet fuel, kerosene, various fuel oils, crude oil, petroleum jelly and some lubricating oils, were identified by gas chromatography of the residue on, e.g., a column of 5% of DC-200 on Gas-Chrom Q temperature programmed from 110 to 224 °C at 10 ° per minute, or a capillary column coated with 0.5 μ m of DC-200 and temperature programmed from 80 to 170 °C at 3 ° per minute, both operated with helium as carrier gas and flame ionization detection, or a column of 5% of QF-1 and 3% of DC-200 on Gas Chrom Q operated at 180 °C with ^{63}Ni electron-capture detection. For heavier products, the pentafluorobenzyl derivatives were used for gas chromatography.

Jeltes and den Tonkelaar⁴³ investigated problems of oil pollution, the nature of the contaminants and the chemical methods of oil pollution, the nature of the contaminants and the chemical methods used for their detection. In particular, the use of gas chromatography to obtain 'fingerprint' chromatograms of oil pollutants in water, and of infrared spectrophotometry to determine the oil contents of soils and sediments, is discussed.

Ahmadijian and Brown⁴⁴ investigated the feasibility of remote detection of water pollutants and oil slicks by laser-excited Raman spectroscopy. They showed that, by use of a system of lenses and mirrors, laser-excited Raman spectra can be recorded for samples containing oil at a distance of 21 ft from the instrument.

McMullen *et al.*⁴⁵ discussed the principle and operation of a system to detect and measure the pollution of water surfaces by oil. The apparatus, which is described in detail with the aid of photographs and drawings, utilizes buoyant sampling heads which float on the water surface to record surface tension changes caused by the presence of either soluble or insoluble monolayers. A battery-operated central control unit and pen recorder are attached at the end of a 60 ft floating cable, and a trigger circuit can be used to activate an alarm when surface tension changes are detected. Field trials, using oil as the polluting agent, on various canals are reported, and it is concluded that the apparatus could be used for the detection of detergent and crude sewage pollutants.

Jeltes *et al.*⁴⁶ have applied capillary gas chromatography to the analysis of hydrocarbons in water and soil. The advantages in capillary columns over packed columns in obtaining practically useful information on environmental pollution by hydrocarbons was demonstrated by these workers. Improved separation on capillary columns gives fine-structured chromatographic fingerprints useful for source recognition. These workers pointed out that the ratios of *n*-alkanes and isoprenoids are important in studies of biodegradation of oil pollution. The compounds were not separated on packed columns.

Cole⁴⁷ has investigated the use of gas chromatography in the identification of slop oils resulting from oil refinery leaks. Oils leaking into the waste-water system were examined by gas chromatography on a column (6 ft \times 0.25 in. o.d.) of 20% of SE-52 on silanized Chromosorb W (60–80 mesh) temperature programmed from 50 to 300 °C at 15° per minute, with nitrogen (60 ml min⁻¹) as carrier gas and flame ionization detection; and by infrared spectrophotometry. Reference is then made to a library of the results of similar tests on samples of all the refinery process streams. Only one ml of oil sample is required, and identification normally takes less than 1 hour.

Vos *et al.*⁴⁸ have carried out a detailed study of the analysis of oil contaminated ground water to ascertain the rate of filtration of oil components, and the effects of their biodegradation, under conditions very close to those in a natural aquifer. Large scale lysimeter experiments are reported in a sand dune area where the ground-water level could be adjusted with an external overflow device. Details are given of hydrocarbon concentrations determined by adsorption onto Amberlite XAD-4 resins, and investigations using gas chromatography, mass spectroscopy, high resolution gas chromatography, infrared spectroscopy and ultraviolet spectroscopy.

Garria and Muth⁴⁹ have used gas chromatography to characterize crude, semi-refined, and refined oils.

Characterization of oils in the marine environment

In the marine environment gas chromatography has been employed to identify petroleum products.^{12,21,28,34,35} Here the pollutants are crude oil, marine residual fuel oil and crude oil sludge consisting of a concentrated suspension of high-melting-point paraffin wax in crude oil. Although weathering of marine oil pollutants can be such that the oil is rendered unrecognizable, the time required to achieve this was found to be so long as to be insignificant in regard to pollutant identification.³⁵ Ramsdale and Wilkinson²⁸ employed a specially constructed injection device which permitted direct introduction of samples contaminated with water, seaweed, sand, or sediments. Pollutants were generally readily identified.

Occasionally the mound of unresolved components on the chromatogram supporting the superimposed *n*-alkane peaks, confuse the true *n*-alkane profile. This has been overcome by separating off the *n*-alkanes using molecular sieves, prior to g.c.³⁴ However, separation of *n*-alkanes in this way, or by urea complex formation,³⁶ is reported as being more applicable to distillates rather than residual materials, and also the separation is not entirely specific.³⁵ In the case of marine pollutants it has been found advantageous to chromatograph a distilled residue, b.p. > 343 °C³⁴, or fraction, b.p. 245–370 °C,²⁰ which avoids problems caused by evaporation of lower ends by weathering.

Chromatograms of marine pollutants have been published; crude oils, 200 second fuel oil, 2000 second fuel oil, pollution samples;³⁴ sludge wax, crude

oil sludge, Bahrein fuel oil, 3000 second diesel fuel, pollution samples;²⁸ marine diesel fuel, sludges, crude oil, residual fuel oil.²⁰

Freegarde *et al.*⁵⁰ have discussed the identification, determination, and ultimate fate of oil spilt at sea.

Erhardt and Blumer⁵¹ have developed a method for the identification of the source of marine oil spills, by gas chromatographic analysis and results for eight different crude oils are given. Distinguishing compositional features are still recognizable after weathering for more than 8 months. The method was used for the tentative source identification of samples of beach tar.

Zafirion *et al.*⁵² have shown that commercial oil spill emulsifiers can interfere with the gas chromatographic detection of the source of oil spills.

Boylan and Tripp⁵³ determined hydrocarbons in sea water extracts of crude oil and crude oil fractions. Samples of polluted seawater and the aqueous phases of simulated samples (prepared by agitation of oil-kerosene mixtures and unpolluted seawater to various degrees) were extracted with pentane. Each extract was subjected to gas chromatography on a column (8 ft \times 0.06 in.) packed with 0.2% of Apiezon L on glass beads (80–100 mesh) and temperature programmed from 60 to 220 °C at 4° per minute. The components were identified by means of ultraviolet and mass spectra. Polar aromatic compounds in the samples were extracted with methanol-dichloromethane (1:3).

Investigations on pelagic tar in the North West Atlantic have been carried out by Bulten *et al.*⁵⁴ using gas chromatography. Their report collects together the results of various preliminary investigations. It is in the Sargasso Sea, where the highest concentrations (2–40 mg m⁻²) occur, and on beaches of isolated islands, such as Bermuda. These workers discuss the occurrence, structure, possible sources, and possible fate of tar lumps found on the surface of the ocean.

Zafirion and Oliver⁵⁵ have developed a method for characterizing environmental hydrocarbons using gas chromatography. Solutions of samples containing oil were separated on an open-tubular column (50 ft \times 0.02 in.) coated with OV-101 and temperature programmed from 75 to 275 °C at 6° per minute; helium (50 ml min⁻¹) was used as carrier gas and detection was by flame ionization. To prevent contamination of the columns from sample residues, the sample was injected into a glass-lined injector assembly, operated at 175 °C, from which gases passed into a splitter before entering the column. Analysis of an oil on three columns gave signal-intensity ratios similar enough for direct comparison or for comparison with a standard. The method was adequate for correlating artificially weathered oils with sources and for differentiating most of 30 oils found in a sea port.

The identification of hydrocarbon oil spills poses a difficult analytical problem. Not only are these samples extremely complex but, in many cases, there are only slight differences in their compositions. The action of the environment is another complicating factor that changes compositions by the loss of light ends, the action of microbes, the action of sand and sea water, and contamination by other organic matter.