# The analysis of oil-contaminated groundwater




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## Introduction

The effect of a spillage of mineral oil onto soil and the consequences for groundwater and drinking water resources is currently being investigated [1] in the Netherlands by the 'Contactcentrum Olie-industrie - Openbare Watervoorziening' (Oil Industry/Public Water Suppliers Contact centre, COOW). The COOW has been set up as an organ of co-operation between the oil companies (through Stichting CONCAWE) and the association of Dutch drinking-water suppliers (VEWIN) on matters of mutual concern:

in particular, the possible contamination of drinking water resources as a result of oil spillage.

Large-scale lysimeter experiments are being carried out in the dunes near Katwijk, The Netherlands, at the production location of the NV Leidsche Duinwater Maatschappij. The purpose of the study is to ascertain the rate of infiltration of the oil components, and the effects of their biodegradation, under conditions very close to those in a natural aquifer.
The lysimeter is a concrete construction consisting of twelve compartments, tanks with a cross-sectional area of 2 x 2 m and a height of 5 m. These tanks are open at the top and filled with dune sand.
The lower 3 m of the sand 'columns' represents the natural environment in the Dutch dunes. At the start of the experiment a 30-cm dune sand layer on top of the 3-m layer was artificially contaminated with gas oil or with a mixture of model hydrocarbons representing a gas oil. This 'oil pancake' was then covered by a top layer of 100 cm clean dune sand planted with beach grass.
The sand columns are subjected to natural rainfall. Their height and porosity correspond to an average movement of the rainwater front over a period of three years. The groundwater level is adjustable with an external overflow device. The level is maintained so that the oil pancake is normally in contact with groundwater and that water samples can be drawn from 5 cm below it. Further sampling connections are mounted at various depths, corresponding to the average progress of the rainwater front after ½, 1, 2 and 3 years. At these intervals samples are drawn from each lysimeter column and analysed.
This article sets forth the standardized analytical methods used and goes on to describe experimental procedures for obtaining further information on the water samples drawn.

## Waarom Engels?

Bijstaand artikel wordt in de Engelse taal gepubliceerd, omdat er grote waarde aan wordt gehecht dat zoveel mogelijk collega's in binnen- en buitenland geattendeerd worden op het kostbare onderzoek dat hier in Nederland op dit terrein wordt verricht. Zo hoopt men te voorkomen dat elders in de wereld soortgelijk onderzoek gedaan zou worden, hetgeen als verspilling van energie en geld wordt beschouwd. Zoals bekend is publikatie in $H_2O$ van artikelen in een andere taal dan de Nederlandse uitzondering. Dit artikel is de uitzondering die de regel bevestigt, dat dit tijdschrift slechts Nederlands-talige artikelen publiceert.

## Analytical approach

An investigation into the fate of mineral oil in soil and, more specifically, of groundwater contaminated with the oil may be expected to involve a rather extensive analytical effort. The measurement of what may be called primary contamination: the occurrence of dissolved hydrocarbon components, mainly the lower aromatics, in the water samples, is relatively simple. Straightforward routine analyses can also be used to determine some of the secondary effects: changes in number of bacterial cells; depletion of dissolved oxygen; appearance of ions typical of a reducing environment such as $NH_4^+$, $NO_2^-$, $Fe^{2+}$, $Mn^{2+}$ and $S^{2-}$; and, finally, tainting of the taste of the water, which may be considered the key effect of this type of groundwater pollution.
Analytically more complex is the detection and identification of the organic (bio)-chemical oxidation products formed, not least because they are wide in variety but low in concentration.

The following section briefly describes the standard routine analyses being carried out on the water samples from the lysimeters. The determination and identification of the organic compounds and oxydation products will be dealt with subsequently.

### Standard analytical methods

The routine analytical methods being used in the lysimeter investigation are listed and described very briefly. If a standardized procedure is being followed the method is indicated in the title [2, 3, 4].

1. *Temperature*
Two lysimeters are provided with two platinum resistance thermometers at each sampling depth.

2. *pH* (ASTM-E70)
Usual potentiometric measurement at sampling temperature.

3. *Dissolved Oxygen content* (ASTM-D 1589)
Polarographic Beckman Fieldlab Model 008 Oxygen Analyzer with electrode mounted in a flow cell.

4. *Baterical cell count* (Standard Methods No. 406, modified)
Aerobic cells are counted by plating $10^2$ to $10^6$-fold diluted samples on Difco plate count agar in duplicate. Incubation at 30 °C for 42 h. Lower limit of detection $10^3$ ml$^{-1}$.

5. *Inorganic Carbon (IC) content* (ASTM-D 2579)
A 20 µl sample is injected into an acid-packed reaction zone of a Beckman Model 915 TOC Analyzer at an oven temperature of 150 °C. The total of $CO_2$ from decomposed carbonates and dissolved $CO_2$ is measured in an infra-red analyser. Organic carbon is not oxidized at this temperature.

6. *Total Organic Carbon (TOC) content* (ASTM-D 2579)
A 20 µl sample is injected into a platinum-catalyst-packed reaction zone of a Beckman Model 915 TOC Analyzer at an oven temperature of 950 °C. $CO_2$ from burned organic compounds and from decomposed carbonates, together with dissolved $CO_2$, is measured in an infra-red analyser. From the Total Carbon (TC) content thus found the IC content is subtracted to give the Total Organic Carbon (TOC) content.

7. *Hydrocarbon content* (CONCAWE Report No. 9/72, Method IIIB)
A 1-l water sample is extracted with 10 ml n-pentane. The extract is stripped of non-

hydrocarbon material by treatment with 1 g Florisil and analysed for hydrocarbons by programmed temperature gas chromatography.

8. *Chemical Oxygen Demand*

a) Dichromate Method (ASTM-D 1252). A water sample is oxidized with a standard chromic acid solution by refluxing at 145 °C for 2 h. Excess dichromate is titrated with a standard ferrous ammonium sulfate solution.

b) Alternatively, the COD can be measured instrumentally with the 'AquaRator' manufactured by Precision Scientific Co. A 20-200 $\mu$l sample is injected into an oven at 850 °C with a platinum catalyst in a $CO_2$ gas stream. Organic and oxidizable inorganic compounds are oxidized by the $CO_2$ and the resulting CO is measured in an infra-red analyser.

9. *Iron content* (ASTM-D 2576)

Determined by atomic absorption spectroscopy on a sample to which nitric acid has been added.

10. *Manganese content* (ASTM-D 2576)

As described under 9.

11. *Electrical conductivity* (ASTM-D 1125)

Measured at 20 °C with a Philips GM 4249/01 conductivity meter.

12. *Nitrite content* (ASTM-D 1254, Method A, modified)

The diazonium compound formed by diazotization of sulfanilamide by nitrite ion at pH 2 is coupled with N-1-naphthylethylenediamine to produce an azo dye. Spectrophotometric measurement at 540 nm is automated in a Technicon 'AutoAnalyzer'. Lower limit of detection: 0.03 mg/l as nitrite-N.

13. *Nitrate content* (Kamphake [5])

The nitrate is reduced at 26 °C with hydrazine to nitrite and determined together with the nitrite already present as described under 12. The nitrate content is calculated by difference. Lower limit of dectection: 0.05 mg/l as nitrate-N.

14. *Ammonia content* (Standard Methods No. 132C)

Reaction with phenol and hypochlorite to indophenol, measured at 610 nm with a Technicon 'AutoAnalyzer'. Lower limit of detection 0.05 mg/l as ammonia-N.

15. *Total Phosphate content* (ASTM-D 515, Method A)

Meta-, pyro- and polyphosphates are first converted to orthophosphate by hydrolysis with nitric acid at 100 °C. Orthophosphates are then converted to a blue molybdenum complex, which is measured spectrophotometrically at 660 nm in the Technicon 'AutoAnalyzer'. Lower limit of detection: 0.06 mg/l as phosphate-P.

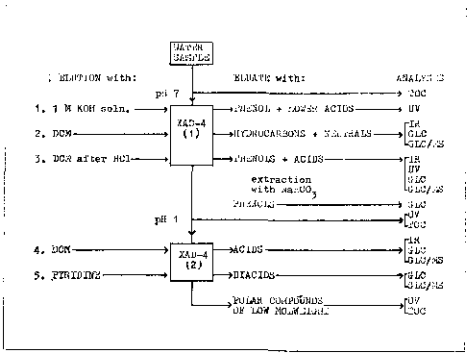



*Fig. 1 - Analytical scheme of adsorption/selective desorption.*

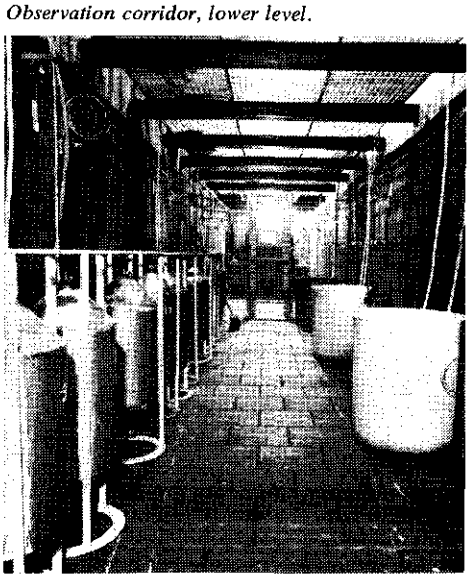
16. *Phenolics content* (ASTM-D 1783)

Spectrophotometric determination at 510 nm of steam-distillable, non-para-substituted phenolic compounds as the 4-aminoantipyrine dye. The analysis is automated with a Technicon 'AutoAnalyzer'. With non-turbid, non-coloured samples the distillation step may be omitted. Lower limit of detection: 0.01 mg/l, expressed as phenol.

17. *Sulfate content*

Coulometric sulfur determination before and after precipitation of sulfate as $BaSO_4$. The sulfate content is calculated by difference. In the determination the sulfate is reduced by a strong HI solution at 120 °C. The $H_2S$ already present or formed is then oxidized to $SO_2$. Finally, the $SO_2$ is titrated coulometrically with iodine.

*Observation corridor, lower level.*



18. *Sulfide content*

The sample is preserved with zinc acetate/caustic. During analysis 1 ml of the sample is dissolved in 6 molar hydrochloric acid at 50 °C. The $H_2S$ liberated is stripped out with $N_2$ and burnt with $O_2$. The $SO_2$ formed is titrated coulometrically with iodine. Lower limit of detection: 0.01 mg/l as sulfide-S.

19. *Organic Nitrogen content* (Standard Methods No. 135)

Ammonia is stripped out and organic N is converted into ammonia-N by Kjeldahl destruction. After addition of caustic the ammonia is distilled off, absorbed in a standard boric acid solution and titrated with hydrochloric acid. Lower limit of detection: 0.2 mg/l N.

N.B. It has been found that organic N cannot be determined reliably at low concentrations when a sample also contains nitrates.

20. *Taste number*

The taste number is the dilution ratio at which the taste of a water sample is just no longer detectable. Dilution water is taken from a non-contiminated (blank) lysimeter compartment. Testing is carried out by personnel of the NV Leidsche Duinwater Maatschappij at Katwijk.

**Non-standard analytical procedures**

The success of every research enterprise depends in the first place, of course, on the setting up of the experiments. Implicitly, the versatility, sensitivity and reliability of the analyses which must describe the results of the experiments are of prime importance. In the case of this unique lysimeter project, therefore, it seemed worth while to draw up an analytical scheme for collecting as much information as possible on the organic components in the water samples drawn. In view of the wide variety of hydrocarbons and their oxidation products to be expected in the lysimeter samples, and the very low concentrations, the procedure decided upon was:

1. to concentrate the compounds by adsorption;

2. to desorb the concentrated compounds selectively in specific groups;

3. to aim for identification of the compounds within each group as far as possible.

The idea is probably most easily explained by showing the analytical scheme right away (fig. 1).

The diagram indicates which types of compounds are adsorbed on the first resin column from the water sample as it runs

from the lysimeter at pH 7. The figure further depicts how three groups of compounds are desorbed in sequence by 1) a 1 molar KOH solution in water, 2) dichloromethane (DCM) and 3) DCM after acidification of the adsorbates. From the third group the phenols can be isolated by extraction with a molar bicarbonate solution. The analyses to which the various extracts are subjected are given in the last column. GLC analysis or separations are often done after silylation of the extracts.
The mono- and dicarboxylic acids which are not adsorbed on the first column because they are too highly soluble in water at a pH of 7 are adsorbed on the second at pH 1. They are separated in the next step by elution with first DCM and then pyridine. Very polar compounds, most of which have a low molecular weight, are not adsorbed, even on the second column. The recoveries in both adsorption steps are checked by TOC measurements.
The procedures and analytical methods used are described in further detail below.

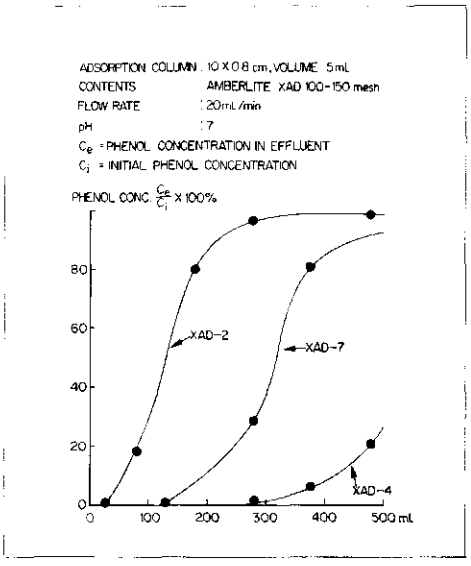



*Fig. 2 - Adsorption of phenol on amberlite resins: break-through curves for 10 mg/l solutions.*

**Adsorption and desorption**

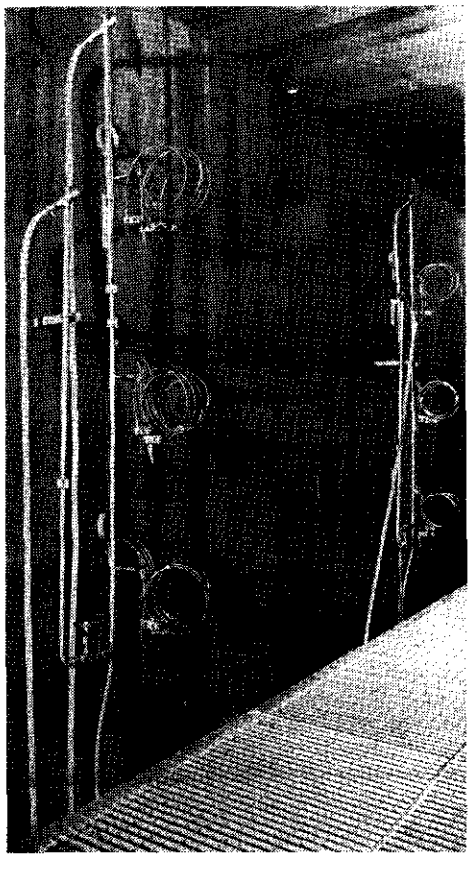
*Choice of the adsorption resin*

The choice of the Rohm & Haas Amberlite XAD-4 resin for the analytical purposes described was made on the basis of the literature [6, 7] available and the results of some work preparatory to the actual lysimeter work. Since three resins seemed most suitable for water analysis it was decided to compare the non-polar XAD-2 and XAD-4 resins (polystyrene/divinylbenzene) with the slightly polar XAD-7 resin (polyacrylate) in tests with 10 mg/l aquous phenol solutions. The break-through curves and the experimental conditions are presented in fig. 2.
The XAD-4 resin proved the most suited to the purpose, probably as a result of its high specific surface area: 780 $m^2g^{-1}$.
(A check on the overall suitability of this resin in adsorption/ selective desorption separations is presented at the end of this section.)

*Preparation and use of Amberlite XAD-4*

Before use the XAD-4 is ground and sieved. The 60-100 mesh fraction is then extracted twice with diethyl ether in a Soxhlet, first for 4 h and then for 16 h. The ether is removed on the steam bath and the resin kept under methanol. The XAD-4 is then placed in an adsorption tube and washed with demineralized water until the TOC of the drain water is less than 1 mg/l.
In the lysimeter work 5 ml (= 1.5 g dry weight) of clean resin is put in a Pyrex glass adsorption tube of 10 x 0.8 cm. The water flow rate is set not to exceed 20 ml/min. For the sampling of lysimeter water a first adsorption tube containing XAD-4 is joined direct to the sampling connection so as to avoid evaporation of light compounds. Consequently the water sample cannot be acidified to pH 1 before adsorption and the effluent of the tube still contains part of the carboxylic acids. Therefore, this effluent is collected, adjusted to pH 1 with HCl and then passed through the second XAD-4 column in the scheme, which is identical to the first. This is good practice since the volatile hydrocarbons were already adsorbed on the first column.

*Observation corridor upper level, with overflow pipes and sampling connections.*



*Selective desorption of organic compounds*

In general, the compounds most soluble in water are adsorbed the least and, once adsorbed, are the first to be desorbed.
In the process of selective desorption the adsorbates are 'manipulated' in two ways: 1) by adjustment of the pH and 2) by choice of the proper elution solvent.
The procedure for concentration/separation as depicted in fig. 1 is the following.
5 l water is passed direct from a lysimeter sampling connection through the first XAD-4 column. The dissolved organic material is adsorbed there, except for the lowest molecular weigt mono- and dicarboxylic acids and other very polar compounds. In principle, a first group of compounds comprising *phenol and lower acids* can be isolated from the adsorbate by elution with 20 ml of a 1 M KOH solution in water. In the case of the lysimeter samples, however, these compounds have not in fact been found, because they either have not been present or have been adsorbed only to a limited extent when the 5-l water sample has been passed through 5 ml resin. Lower acids can be adsorbed in the form of their salts at pH 7, but only from much smaller water samples. The concentration factor attained upon desorption, and hence the sensitivity of the determination, is then correspondingly lower.

A *hydrocarbons and neutrals* group (alcohols, ethers, esters, etc.) is subsequently desorbed from the still alkaline column by DCM. This eluate is analysed by IR spectroscopy (neutrals) and subjected to routine programmed temperature gas chromatography (hydrocarbons and part of the neutrals). GLC analysis of the eluate after silylation is used to study the alcohols in particular. It is clear that the results obtained in this desorption step can be compared with those from the hydrocarbon content analysis mentioned as No. 7 in the section on 'Standard analytical methods'.
The third group of compounds, *phenols and acids*, is finally desorbed with 5 ml DCM after the column has been acidified with 10 ml concentrated hydrochloric acid.
The eluate is studied by GLC and GLC/MS after silylation. A 1-ml portion of the eluate is further extracted with 1 ml of 1 M solution of sodium bicarbonate in water. The phenols then remain in DCM solution and are determined by GLC after silylation.

The amount of acids in this group is then computed by difference.

*Discussion*

As has already been mentioned, the stronger, mainly aromatic, *acids* and the *dioic acids* can be adsorbed at pH 1 on a second XAD-4 column. (The *acids* group includes those lower acids which were not adsorbed in salt form at pH 7 on the first column.) They can subsequently be separated by desorption with DCM followed by pyridine. Some of the compounds within both groups are identified by IR spectroscopy and, after silylation, by GLC and GLC/MS analysis.

A relatively small group of very polar compounds of low molecular weight is not adsorbed, even onto the second XAD-4 column. For making up the balance this filtrate is subjected to TOC analysis.

UV spectroscopy is used to check whether any aromatic compounds have slipped through the second XAD-4 column.

The analysis of amines was not studied in the context of lysimeter water analysis because they were not expected in the samples. Junk [7] reports that amines are adsorbed onto XAD and that they are recovered in an acidic eluate. In the analytical scheme shown in fig. 1 they must therefore be expected in group 3. There is a possibility that higher molecular weight amines will be eluted by DCM at pH 7, in which case they will show up in group 2 as *neutrals*.

*Check on the adsorption/selective desorption scheme*

To check the effectiveness of the concentration, separation and analysis described above, 5 l of a synthetic effluent was made up with a variety of compounds, thirteen in number, dissolved in demineralized water, each at 1 mg/l. The compounds and the outcome of this model experiment are given in table I.

As mentioned earlier, phenol and the acids lower than $C_6$ in the lysimeter water samples are not determined. The other results are better.

The separation into the various groups is good. The recovery of most compounds is at least reasonable, bearing in mind that further refinement can be introduced during the lysimeter programme. The first indication from practice of where such a refinement may be needed is that, at the high pH in the first desorption step of the first XAD-4 column, ketones and aldehydes may react. There are signs that when either one or both of these types of compounds are present the base/acid separation cannot be carried out and both groups must be worked up together.

TABLE I - *Analysis of a synthetic water sample.*

| Compound | Recovery (%) within each group of compounds | | | | | Total recovery, % |
|---|---|---|---|---|---|---|
| | Phenol + lower acids | Hydrocarbons + neutrals | Phenols + acids | Acids | Diacids | |
| Phenol | low | | | low | | low |
| lower acids | very low | | very low | very low | | very low |
| Gas oil | | 100 | 0 | | | 100 |
| Octanol-1 | | 100 | 0 | | | 100 |
| Hexyl acetate | | 100 | 0 | | | 100 |
| o-Propylphenol | | | 71 | 0 | 0 | 71 |
| p-tert-Butylphenol | | | 71 | 0 | 0 | 71 |
| Decanoic acid | | | 77 | 0 | 0 | 77 |
| 2-Naphthoic acid | | | 78 | 13 | 0 | 91 |
| Hexanoic acid | | | 0 | 89 | | 89 |
| Benzoic acid | | | 0 | 85 | | 85 |
| cis-1,2-Cyclohexane-dicarboxylic acid | | | 0 | 0 | 74 | 74 |
| Decanedioic acid | | | 0 | 0 | 93 | 93 |

**High resolution gas chromatography** (HRGC)

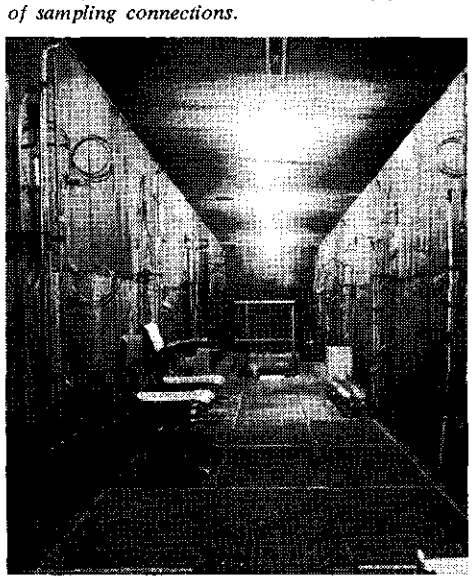
HRGC is used for analysis for hydrocarbons down to very low concentration levels. Table II provides an example of results obtained with a sample of water which had been in contact with gas oil for several days. About 50 compounds could be identified, some down to the $\mu$g/l concentration level. The procedure is described below.

**Analytical methods**

1. *Gas chromatography*

GLC analyses are carried out with a dual-column, dual-FID HP 7621 A gas chromatograph equipped with an automatic sampler and a programmed temperature oven. Stainless steel columns of 180 x 0.3175 cm OD are used with 3 %w Silicone gum OV-1 on Gas-Chrom Q of 100-200 mesh. Chromatograms are measured by a digital integrator linked to a teleprinter. The printout is simultaneously recorded on punch tape so that retention times and Kovats indices can be calculated by computer.

*Detail of summer- and winter-overflow pipes and of sampling connections.*



2. *Mass spectroscopy*

During some of the GLC analyses, MS is carried out on-line with a Varian MAT-111.

3. *High resolution gas chromatography*

HRGC is carried out with a GLC equipped with a capillary analysis column and a packed preseparation column which provides for flushing > 99 % of the solvent and injecting the remainder in one batch.

The columns are connected valveless as described by Deans [8]. The instrument used is a Packard-Becker model 419 GLC with a 100 x 0.3175 cm OD precolumn packed with Dexsil 300 GC and 50 m x 0.25 mm ID analysis column, wall-coated with Silicone oil OV-101.

The carrier gas is nitrogen. The precolumn is heated ballistically from 30 °C to 280 °C, the analysis column at the constant rate of 4 °C/min from 30 °C to 250 °C.

4. *Infra-red spectroscopy*

Eluates in DCM are measured at about 1700 $cm^{-1}$ and 3600 $cm^{-1}$ for carbonyl/carboxyl and hydroxyl groups. Semi-quantitative information is obtained using mean molar absorptivities of 400 l $mol^{-1}$ $cm^{-1}$ for carbonyl and 80 l $mol^{-1}cm^{-1}$ for hydroxyl groups. The values originate from calibration runs with a number of relevant model compounds.

5. *Ultraviolet spectroscopy*

In the lysimeter experiments with gas oil UV spectroscopy is used to measure mono-, di- and triaromatics in the n-pentane extracts of the oil in water determinations after treatment with Florisil. The n-pentane extracts of water samples from the experiments with the mixture of model hydrocarbons, after treatment with Florisil, were found to contain almost exclusively 2-methylnaphthalene. This means that spectra can be read at 223 and 270 nm and molar absorptivities of 121,000 and 4,570 l $mol^{-1}cm^{-1}$, respectively, are

TABLE II - *Hydrocarbons content of water contacted with 10 %v gas oil*
(as determined by High Resolution Gas Chromatography)

| Component | Conc., mg/l |
|---|---|
| Benzene | 0.36 |
| Toluene | 0.61 |
| n-Octane | 0.016 |
| Ethylbenzene | 0.13 |
| 1,4-Dimethylbenzene<br>1,3-Dimethylbenzene | 0.44 |
| 1,2-Dimethylbenzene | 0.24 |
| n-Nonane | 0.004 |
| Isopropylbenzene | 0.011 |
| n-Propylbenzene | 0.022 |
| 1-Methyl-3-ethylbenzene | 0.079 |
| 1-Methyl-4-ethylbenzene | 0.029 |
| 1,3,5-Trimethylbenzene | 0.054 |
| 1-Methyl-2-ethylbenzene | 0.056 |
| Tert-butylbenzene<br>1,2,4-Trimethylbenzene | 0.19 |
| Isobutylbenzene<br>n-Decane | 0.003 |
| sec-Butylbenzene | 0.007 |
| 1-Methyl-3-isopropylbenzene<br>1-Methyl-4-isopropylbenzene | 0.012 |
| 1,2,3-Trimethylbenzene | 0.11 |
| Indan | 0.020 |
| 1-Methyl-2-isopropylbenzene | 0.002 |
| 1,3-Diethylbenzene | 0.005 |
| 1-Methyl-3-n-propylbenzene | 0.013 |
| n-Butylbenzene<br>1-Methyl-4-propylbenzene | 0.007 |
| 1,2-Diethylbenzene | 0.004 |
| 1,3-Dimethyl-5-ethylbenzene<br>1,4-Diethylbenzene | 0.020 |
| 1-Methyl-2-propylbenzene | 0.012 |
| 1,4-Dimethyl-2-ethylbenzene | 0.026 |
| 1,3-Dimethyl-4-ethylbenzene | 0.026 |
| 1,2-Dimethyl-4-ethylbenzene | 0.034 |
| 1,3-Dimethyl-2-ethylbenzene | 0.004 |
| 1,2-Dimethyl-3-ethylbenzene | 0.006 |
| 1,2,4,5-Tetramethylbenzene | 0.020 |
| 1,2,3,5-Tetramethylbenzene | 0.032 |
| 5-Methylindan | 0.029 |
| 1,2,3,4-Tetramethylbenzene | 0.12 |
| 4-Methylindan | 0.032 |
| Tetralin | 0.046 |
| Naphthalene | 0.39 |
| 2-Methylnaphthalene | 0.27 |
| 1-Methylnaphthalene | 0.22 |
| Biphenyl | 0.026 |
| 2-Ethylnaphthalene | 0.039 |
| 1-Ethylnaphthalene | 0.027 |
| 1,4-Dimethylnaphthalene | 0.024 |
| Balance | 0.42 |
| Total | 4.2 |

applied in the calculation of concentrations. Within group 3 *'phenols and acids'* total phenols are determined after evaporation of the DCM solvent from 1 ml of the eluate and redissolving the residue in 5 ml of a 60/20/20 (by volume) mixture of water, ethanol and isopropyl alcohol. Phenols are then measured at a pH of 12 at 290 nm, half of the solution being adjusted to pH 8 and used as compensation for the acids present. The phenols concentration is calculated applying a molar absorptivity of 3000 l $mol^{-1}cm^{-1}$. In the conversion from molar to weight concentrations 94, the mol.wt. of phenol, has been adopted as the molecular weight and thus results are expressed 'as phenol'.
All aqueous solutions and the KOH eluate from the first XAD-4 column are subjected to UV spectroscopy as a check on the completeness of the adsorption and on the occurence of phenols.

6. *Silylation*

The following standard procedure is adopted for silylation of samples in DCM or pyridine.
100 $\mu$l sample
10 $\mu$l hexamethyldisilazane
20 $\mu$l trimethylsilyldiethylamine
20 $\mu$l bis [trimethylsilyl] acetamide
are mixed in a 200 $\mu$l GLC sample tube and kept at room temperature for at least 4 h before being injected into the GLC.

7. *Drying of solutions in pyridine*

Of 25 ml solution, 22 ml is distilled off (azeotrope with water, bp 93 °C) and the residue is made up to 5 ml which then contains 0.3 % water. This water concentration does not interfere with silylation since silylation agent is present in excess.

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