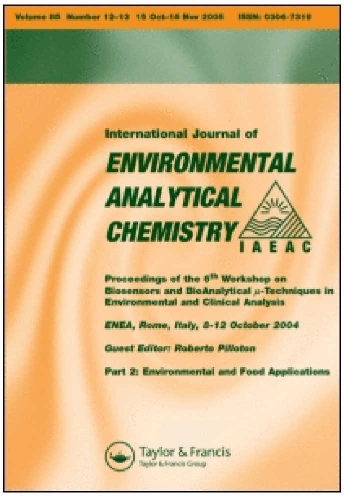

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Determination of Total Hydrocarbons in Water†

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It is important to the oil refining industry to obtain accurate and reliable data on the levels of hydrocarbons in aqueous discharges. However, considerable difficulties are presented in placing data from different locations on a comparable basis, because of the number and diversity of procedures used. The analytical principle involved may differ, for example infrared spectroscopy as opposed to gravimetric determination. Other aspects of the procedures, such as standardisation and calculation, may also vary. A CONCAWE task force of experts from the oil refining industry has identified certain key technical elements to the determination of hydrocarbons in water. The task force concluded that infrared spectroscopy is the best available analytical technique and that any procedure used should include a solvent extraction step, separation of non-polar material and measurement at three wavelengths with the use of typical absorptivities for the calculation of oil-in-water values.

KEY WORDS: Hydrocarbons, oil-in-water, analysis, determination, infrared

INTRODUCTION

The oil refining industry has made substantial reductions in recent years in the total amount of oil and other components of crude oil discharged in aqueous effluents.[1,2] This information has been obtained from sources within the industry and such surveys have clearly shown that a variety of methods are used to determine oil-in-water (i.e. dissolved and suspended hydrocarbons) and other parameters. These methods are used routinely by refinery laboratories and, while the variation in analytical procedure does not affect the overall trend, it is clearly desirable that analytical methods are placed on a comparable basis in order to obtain more accurate

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estimations of the amounts of oil discharged. It must be emphasised that this report is concerned with the overall discharge of oil-in-water and not with the determination of individual trace substances derived from crude oil. Techniques for such, more detailed, analyses are under current investigation by a separate CONCAWE group of experts.

Accordingly, CONCAWE established a special task force of experts, with experience in analysis of oil-in-water in refinery discharges, with the objective of identifying the key technical elements of an analytical procedure for determination of oil-in-water. CONCAWE had previously recommended[3] the use of techniques based on infrared (IR) spectroscopy and the present task force confirmed this recommendation. The survey was therefore limited to IR based methods, including at least thirteen different procedures in current use in Western European refineries. As CONCAWE is not a standardisation body the study excluded the possibility of developing a new standard procedure.

TECHNICAL ASPECTS OF DETERMINATION OF HYDROCARBONS IN WATER

Considerable difficulties are presented in selecting a single method, because of the variable nature of oil and because of the vast range of components, from gaseous hydrocarbons to bituminous compounds and from paraffinic to aromatic hydrocarbons. Further, these components can vary both within different crude oils and, particularly, within oily wastes as a result of different processing conditions. This situation is illustrated in Figure 1 which shows the differences in the IR spectra of toluene, cyclohexane and *n*-heptane. Thus it was accepted at the outset of the study that no approach could be identified which could give an absolute measure of oil-in-water. After careful consideration of a number of published procedures the following technical elements were identified.

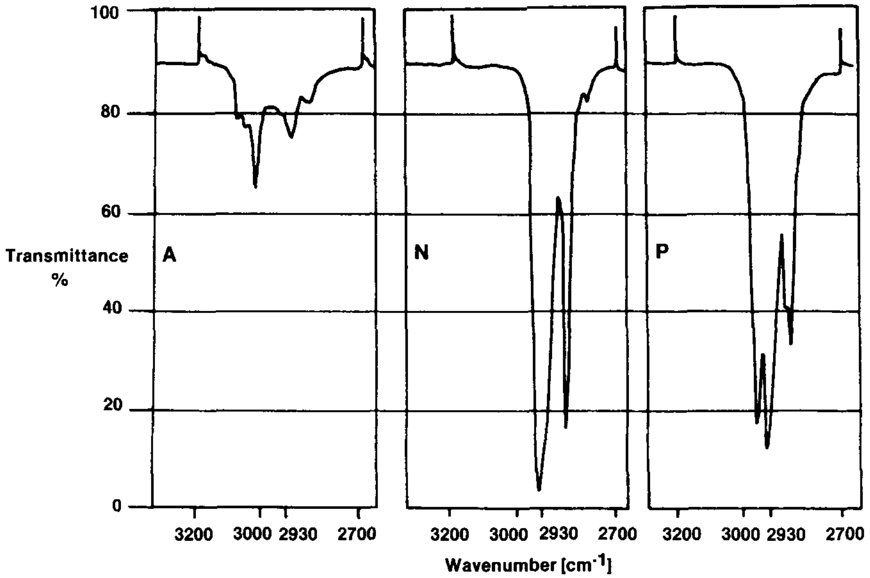
SOLVENT AND SOLVENT EXTRACTION PROCEDURE

The choice of solvent is affected by several aspects including: the recovery of hydrocarbons from the water sample; the possibility of loss of solvent by evaporation with the consequent concentration of hydrocarbons; and the requirements for health and safety in the workplace. Two solvents are generally used: carbon tetrachloride which is less volatile than the other, Freon 113, the use of which has been recommended on grounds of its lower toxicity.[4]

IR TRACES FOR PURE HYDROCARBONS

(25 mg in 100 ml CARBON TETRACHLORIDE)

from Palmer (1980)



A = TOLUENE (AROMATIC)
N = CYCLOHEXANE (NAPHTHENE)
P = n-HEPTANE (PARAFFIN)

FIGURE 1

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REMOVAL OF INTERFERING COMPOUNDS

This aspect is of particular importance where contamination may arise from compounds not originating from the oil refining industry. These compounds are generally polar in nature. The separation of the non-polar hydrocarbons from the polar compounds is generally achieved by use of an appropriate adsorbent either by direct addition of the adsorbent to the solvent, following extraction, or by elution through a column. Experience has shown that it is not possible to carry out this step without simultaneously adsorbing some hydrocarbons (higher molecular weight aromatics). Such compounds generally comprise only a minor proportion of the hydrocarbons in any aqueous sample and any reduction in the value of oil-in-water is much less than the relatively massive distortion that can arise from extraneous material which is removed by this step.

ABSORPTION WAVELENGTHS

The use of infrared spectrophotometry is based on the identification and quantitative measure of absorption by particular chemical groups at characteristic wavelengths. For hydrocarbons, the characteristic groups are (Table I): CH (aromatic) at 3.30 μm (3030 cm^{-1}); $>CH_2$ (methylene) at 3.42 (2924); and CH_3 (methyl) at 3.38 (2958). All of these groups are also present in a vast number of other non-hydrocarbon compounds and, accordingly, it is necessary to include extraction and separation steps in the analytical procedure, as described above.

TABLE I
Absorption wavelengths of characteristic groups in hydrocarbons

	μm	cm^{-1}	Characteristic
CH_2	3.30	3030	Low molecular weight aromatics
$>CH_2$	3.42	2924	Long straight chain saturated hydrocarbons and cycloalkanes
CH_3	3.38	2958	Saturated hydrocarbons

Of the three chemical groups indicated CH is most characteristic of low molecular weight aromatic hydrocarbons. In the higher aromatic homologues the C atoms are partially or wholly substituted. The $>CH_2$ group is mostly present in long straight chain saturated hydrocarbons and in cycloalkanes, and CH_3 is the terminal group of saturated hydrocarbons, although it can be present as a substituent in other compounds.

Consequently the measure of absorbance at three wavelengths, or the overall IR spectrum including these wavelengths, can be used both as a quantitative measure of the hydrocarbons in the sample and as a qualitative evaluation of its composition.

REFERENCE MATERIAL

The choice of reference material in an analytical procedure is of particular importance where a broad group of compounds is to be collectively determined. "Known oils", such as those recovered from the oil separators in a water treatment system, are often used to give measurement of the concentration of oil in aqueous effluents. The relevance of the use of "known" oil may change with the pattern of crude used and with the different processes operating within a single refinery. Nevertheless, reasonable knowledge of the amount of oil discharged from a refinery can be obtained, providing the "known" oil used is a representative long-term composite sample. However, the composition of all such separated oils (also known as "slop" oils) is different from the mixture of hydrocarbons in the water. This is particularly true where further treatment stages, such as air-flotation and biotreatment, are included, owing to selective removal and degradation and the differing distribution of individual hydrocarbons between the oily and aqueous phases. In addition, it may be difficult to compare analytical results obtained by different refinery laboratories as "known" oils will necessarily differ from one refinery to another.

The use of a "reference oil", consisting of a defined mixture of hydrocarbons such as benzene, isooctane and cetane (*n*-hexadecane), does enable comparison of data obtained by different laboratories, including checking of procedures by control authorities. Although this enables the same reference mixture to be used consistently and at different locations, the mixture selected may be quite different from the oil being measured, with a consequent loss of accuracy. The use of such mixtures has no apparent advantage over the use of typical specific absorption coefficients (typical absorptivities)[5] as described below.

CALCULATION OF RESULTS BASED ON TYPICAL ABSORPTIVITIES

In recent years, particular attention has been paid to the development of accurate procedures for direct calculation of results rather than the use of known oils or mixture of pure compounds. The use of typical absorptivities for measurement of CH, $>CH_2$ and CH_3 is generally accepted as the best approach. The absorptivities are defined as "typical" in that they are intended to be of general application, irrespective of the model of IR apparatus used and operating conditions, that is of the resolution of the bands. The simplicity of application of such typical figures counterbalances the minor accuracy. None of the IR procedures directly measures C atoms fully substituted by groups other than H atoms as there is no IR absorption. Such fully substituted H atoms are widely present in hydrocarbons. In order to take their presence into account, suitable correction factors have been developed.[5] This procedure can be refined by calculating the absorptivities for CH, $>CH_2$ and CH_3 for the individual IR apparatus and operating conditions.[6] While this may require an extra effort at the beginning in each laboratory, it would improve the accuracy and allow a sounder comparison of data from different sources.

The calculation procedure using such absorptivities is based on the single spectra of three single compounds (toluene, *n*-hexadecane, pristane), carefully selected in order to give the best overall fit to a broad range of petroleum products without the use of the correction factors mentioned above. In order to allow for the relatively weak absorption of the CH group, a suitable correction should be calculated for the $>CH_2$ and CH_3 shoulder.

CONTINUOUS ANALYSERS

An important recent trend has been the development of apparatus that allows continuous recording of oil-in-water levels. Although such analysers have many practical drawbacks this approach could eventually allow a reduction in the routine laboratory work and the compilation of a much more substantial data base on a cost-effective basis. At the moment such methods are based on IR stream analysers which measure only $>CH_2$ absorption. Consequently, these instruments may be of use for monitoring performance of treatment systems within a single refinery but do not allow compilation on a broader basis of accurate data on the amount of oil discharged by oil refineries.

CONCLUSIONS

The CONCAWE task force has concluded that infrared spectroscopy provides the best basis currently available for the measurement of oil-in-water. Any method that is used should incorporate a solvent extraction step, separation of non-polar material by elution through an adsorbent column and measurement of the hydrocarbons at three wavelengths characteristic of the three predominant groups CH, $>CH_2$ and CH_3. For comparative purposes, the most practical approach to the calculation of oil-in-water values is to use typical absorptivities for these groups, with incorporation of a factor to allow for those groups not measured in the infrared. Continuous stream analysers have only specialised application at present and the development of suitable instrumentation for stream analysis of oil-in-water on a comparative basis across the industry remains an objective for future technical innovation.

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