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DETERMINATION OF OIL IN WATER BY ORGANIC CARBON ANALYSIS.(U)
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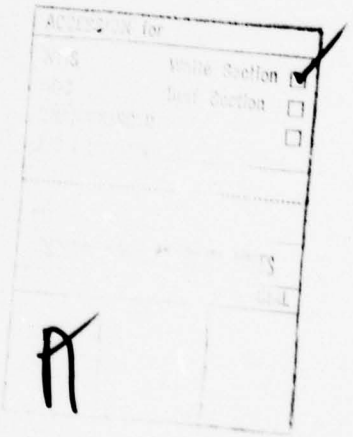

INTRODUCTION

Much recent interest has been shown in the development of rapid methods of determining small quantities of oil in water. The standard method for determination of grease and oil (Ref 1, p. 513) employs partition extraction or Soxhlet extraction with Freon and determines the amount extracted by weighing the residue left after evaporation of the Freon solution. The method most generally used in the laboratory for the analysis of oil in water is a tentative standard method (Ref 1, p. 513), which also employs partition extraction with Freon but determines the amount of oil extracted by infrared spectroscopy using the 2,930 cm^{-1} absorption peak of the aliphatic carbon-hydrogen linkages of the oil (Ref 2). Freon will also extract some non-oily organic materials; if these are polar materials, such as fatty acids or many detergents, the problem can partially be corrected by absorption of these materials on silica gel (Ref 1, p. 520).

Other methods that have been used or studied have measured oil by its fluorescence, by ultraviolet absorption, or by the turbidity or opacity of oily emulsions, but these properties vary for different oils or depend on the particle size of the oil, and they may be affected by other suspended materials. Some of these methods have been automated, but problems have been encountered in obtaining representative samples and in contamination of samples by oil from prior samples.

Another potential method of analyzing oil is by determination of the organic carbon contributed by the oil to the oily water sample. Apparently, this method had received little attention when work was first started at the Civil Engineering Laboratory (CEL). Since that time the method has also been studied at the Naval Academy (Ref 3) and an automated prototype apparatus has been constructed at the Naval Postgraduate School (Ref 4,5).

A potential problem with this method is the difficulty of obtaining a representative and uniform sample. Though this is a problem common to other methods, it may be more important in this case because small samples must be obtained and injected into the organic carbon analyzer. The problem might be solved by homogenizing the oily water sample with an emulsifier and correcting for the carbon added by the emulsifier. The potential usefulness of this method was investigated, and the results are presented in this report.

EXPERIMENTAL WORK

Organic Carbon Analyzer

A Beckman Model 915 Total Organic Carbon Analyzer (Beckman Instruments, Process Division, Fullerton, Calif.) was used for determining carbon contents (Figure 1). The organic carbon content was obtained by subtracting the inorganic carbon from the total carbon. The total carbon channel of this instrument, which converts all carbon to carbon dioxide, had a ceramic combustion tube held at 950°C that contained a cobalt oxide catalyst on pumice. The inorganic channel, which converts carbonates to carbon dioxide, had a Pyrex reaction tube held at 150°C that contained phosphoric acid supported on quartz chips.

The carrier gas was "zero air," containing less than 1 ppm each of carbon dioxide, carbon monoxide, or hydrocarbon. This carrier gas was passed through each channel at 150 ml/min and it served also to regenerate the cobalt oxide catalyst. The samples were injected through injection ports directly into the combustion or reaction tubes with spring-loaded Hamilton syringes (Hamilton Company, Reno, Nev.) having micrometer-adjusted capacities of up to 200 µl. The minimum time between injections was 3 minutes for samples of 50 µl or greater and 2 minutes for samples 35 µl or smaller. The syringe was always inserted in the same rotational position and was removed 7 seconds after the injection. The carrier gas and reaction products from each combustion or reaction tube passed through a condenser where excess water was removed. The moist air containing the carbon dioxide produced from the sample then passed through a channel select valve and into a nondispersive infrared analyzer (Beckman Model 215B), which produced an electrical signal proportional to the carbon dioxide concentration. This signal was recorded on a 100-mV, 10-inch strip chart recorder (Beckman Model 1005) at a chart speed of 0.1 in./min.

To reduce errors in reproducibility, an average of at least two readings (usually three or more for oily samples) was taken. The chart readings can be decreased by unnoticed small air bubbles in the syringe or increased by lint that may be drawn into the syringe. Thus, peaks with deviations of more than 1 unit from the average for standards, or more than 1.5 units from the average for oily samples, were generally eliminated from the calculations.

The peak height produced by the sample was converted to the carbon content by comparison with a calibration curve of peak height versus carbon content in milligrams per liter. The calibration curve was prepared daily with standard solutions spanning the expected range of the unknown samples (for example, 5, 10, 20, 30, and 40 mg/l), with the same volumes as the samples (25 to 100 µl), with the same carrier gas flow (150 ml/min), and with the same gain setting for the infrared analyzer (which was adjusted for nearly full range for the highest standard solution, typically 40 mg/l). The calibration curves were essentially straight lines at lower concentrations (for example, up to 30 mg/l when 35 µl were injected) but had reduced slopes at higher concentrations, and greater curvatures at higher injection levels.

The standard solutions were prepared from 1,000 mg/l stock solutions. These contained 2.125 grams anhydrous potassium acid phthalate per liter for the organic carbon stock solution, or 4.404 grams anhydrous sodium carbonate plus 3.497 grams anhydrous sodium bicarbonate per liter for the inorganic carbon stock solutions. The demineralized water used for the preparation of the stock solutions and standards was purged with nitrogen to remove carbon dioxide. The residual carbon in this water was about 0.5 mg/l inorganic carbon and about 1 mg/l organic carbon.*

Experiments With Blender

The blender unit was a 10-speed model (sold by Sears, Roebuck and Co. and apparently manufactured by the Oster Co.) with removable blade assembly that fit the 1-quart square Pyrex container furnished or a standard Mason jar. Various preliminary experiments were performed with a variety of oils and emulsifiers. Typically, to 500 ml of demineralized water was added a measured amount of aqueous solution of emulsifier. The solution was stirred to provide thorough mixing without appreciable foam formation, and the total carbon content was determined. A weighed drop of oil was added and was blended at full speed for 2 minutes, and the total carbon content was again determined after the foam disappeared. The results of such an experiment are shown in Table 1. In this experiment, the foam height of the freshly blended oily samples was about 30 mm, and the foam required up to 15 minutes to disappear.

Other experiments were performed with a blender using 1/2-pint Mason jars into which the desired amount of oil and emulsifier were added in hexane solution. The jars were supported at a 45-degree angle in a water bath at 85°C, and 1/2 l/min of nitrogen was blown into the jars for 15 minutes to remove the hexane. To the evaportaed oil and emulsifier was added 100 ml of water, and the blender blade assembly was screwed on top of the jar. The jar was inverted on the blender base and the mixture was blended for 2 minutes at high speed. The jars, with blender blades removed, were allowed to sit for 20 minutes to allow the foam to settle, and the carbon contents of the mixtures were determined. The results of such an experiment are shown in Table 2.

Use of Ultrasonic Probe

Hexane solutions of emulsifier (200 µl each and dispensed with a spring-loaded syringe) were added to a series of 250-ml beakers. Hexane solutions of white mineral oil were pipetted into the beakers in varying amounts. The solutions were evaporated essentially as before except that the beakers were kept in an upright position. Demineralized water was added (100-ml portions), the mixtures were agitated for 2 minutes each with a 300-watt ultrasonic probe (Sonic Dismembrator 300 manufactured by Artek Systems Corporation, Farmingdale, N.Y.), and the mixtures were

*Where appropriate, corrections for these amounts were made in the plotted concentrations of the standard solutions to produce calibration curves that started at the intercept of the axes.

analyzed. The results of such an experiment are shown in Table 3. The average recovery was 68.7%, with a standard deviation, σ, of 6.1 and a relative standard deviation, RDS, of 8.9%.

When a 4.3-mg drop of Navy special fuel oil (NSFO) was added to 400 ml of demineralized water containing aqueous Tergitol 15-S-9 (20.6 mg/l carbon), the black oil on two occasions dropped to the bottom and became well-mixed with a Sonic Dismembrator. The mixtures gave total carbon values of 28.4 and 28.2, carbon in oil values of 7.8 and 7.6, and experimentally determined oil contents of 9.2 and 9.0 mg/l, respectively; for the 10.7 mg/l oil weighed out, these were recoveries of 86% and 84%, respectively. On another occasion a drop of NSFO remained on top of the water and emulsifier and could not be mixed adequately by the Sonic Dismembrator.

Use of Ultrasonic-Mechanical Homogenizer

A Polytron, Type PT-20 (Brinkmann Instruments, Westburg, N.Y.) (Figure 2) was used for the remainder of experiments reported below. This homogenizer has a high-speed motor to which is attached a "generator." The generator consists of a stator (a 20-cm-long, 2-cm-diameter tube with a series of 12-mm-high vertical openings at the bottom end and long vertical openings on two sides) and a rotor (a concentric rod with two 10-mm-high blades at the bottom, held in place with a bearing above the blades). The high-speed revolution of the blades past the openings on the stator provides both shearing action and ultrasonic energy and rapidly circulates the surrounding liquid.

The results of the analysis of intimate mixtures of white mineral oil and emulsifier homogenized with the Polytron are shown in Table 4. Equal quantities of emulsifier (1-ml portions of a solution of 1.14 gm/l in Freon 113) were added to square, 4-oz, wide-mouth bottles, and varying quantities of white mineral oil (none, 1-, 2-, 3-, and 4-ml portions of a 750-mg/l solution in Freon) were added. The solutions were mixed by mild agitation and were evaporated in a water bath at 60°C and kept in the bath under a flow of 500 ml/min of nitrogen for an additional 10 min. To each sample, 150 ml of water was added, and each mixture was homogenized for 1 minute. After settling of the foams, the turbidities of the solutions were measured and the total carbon contents were determined. The average value of the recoveries listed in Table 4 was 81.1% (σ, 4.5; RDS, 5.6%).

Effect of Sample Size on Carbon Analyzer Response

A sample of white mineral oil (15 mg/l) emulsified with Tergitol 15-S-5 (10 mg/l carbon) in demineralized water was injected into the Total Organic Carbon Analyzer in sample sizes of 10 to 70 µl. Care was taken that the front portion of the syringe was inserted in the same position even when micrometer settings were changed. The chart readings for various volumes were:

Microliters	Units
10	23.8
15	31.8
20	40.0
25	47.5
30	55.5
35	62.3
40	68.7
45	74.5
50	78.4
55	83.8
60	85.5
70	97.0

These values are plotted in Figure 3. The slope for a line drawn through the values for samples of 10 to 30 µl was 1.57. The slope for a line drawn through the values for samples of 40 to 70 µl was 0.92. The incremental response per microliter at the higher injection volumes was therefore only 59% as great as it was at the lower injection volumes.

An organic carbon standard solution, containing 20 mg/l of carbon as potassium acid phthalate, was similarly injected. The chart readings for various volumes were:

Microliters	Units
10	16.7
20	29.8
30	42.6
40	54.9
50	66.7
60	78.1
70	88.3
80	98.2

These values are also plotted in Figure 3. The slopes for 10 to 30 µl and 40 to 70 µl are 1.30 and 1.12, respectively; and the latter value is 86% of the former value.

Analysis of Oil in Water

From a 2-ml disposable glass syringe with a 27-gauge needle, a drop of white mineral oil was added to 300 ml of demineralized water in a square, 8-oz, wide-mouth bottle, giving an oil content of about 15 mg/l. The syringe was handled with forceps and was weighed before and after each addition; handling of the syringe without dispensing oil and re-weighing gave weights reproducible within 0.05 mg. To the oily mixture, 2 ml of aqueous Tergitol 15-S-5 (2.28 mg/l, calculated to contain 1,500 mg/l of carbon, which did not dissolve completely but formed a uniform, light, milky suspension) was added with a pipettor having a polyethylene

tip. The mixture was emulsified with the Polytron homogenizer for 1 minute, the foam was allowed to settle, and the total carbon content was measured. From the value obtained, the average carbon content of similarly treated water samples without oil (but less vigorously mixed to produce less foam) was subtracted to give the carbon attributable to the oil. The latter value was multiplied by 1.18 to give the experimentally determined oil content. The results of such an experiment are shown in Table 5. The average recovery was 83.3% (σ, 6.5).

The results of a similar experiment performed without the addition of emulsifier are shown in Table 6. The average recovery was 59% (σ, 17).

The results of an experiment with Navy distillate fuel in demineralized water at concentrations of about 12 and 34 mg/l (1 and 3 drops, respectively) are shown in Table 7. An emulsifier was again used, and the average recoveries were 81% and 70%, respectively.

Results of an experiment with Navy distillate fuel at concentrations of up to 100 mg/l are shown in Table 8.

Some additional experiments were performed with 800 ml of water (instead of the 300 ml of water) in a 1-liter Erlenmeyer flask to produce mixtures of lower oil content.

Analysis of Oil in Seawater

Oily seawater was made by adding about 12 and 34 mg/l of Navy distillate fuel to 300 ml of filtered seawater. After the addition of emulsifier, the mixtures were homogenized as in the previous experiment. The original seawater and the emulsified mixtures were analyzed for total carbon and for inorganic carbon. The inorganic carbon values were subtracted from the total carbon values to obtain the organic carbon contents. From the organic carbon contents of the mixtures were subtracted the 1.85 mg/l organic carbon content of the seawater plus the 7.95 mg/l organic carbon content contributed by the 2 ml of emulsifier added* to obtain the organic carbon contributed by the oil. The results are shown in Table 9. The average recoveries of the two concentrations were 77% and 65%, respectively.

The results of a similar experiment performed with white mineral oil are shown in Table 10. The correction for organic carbon contributed by the seawater and emulsifier was the value found for such a sample. The recoveries for the 15 and 46 mg/l white mineral oil samples were 77% and 69%, respectively.

DISCUSSION

General Principles

The method under study for the determination of oil in water would determine the organic carbon content of the sample that is attributable to the oil and, by multiplying by an appropriate factor, to convert this

*The 7.95 mg/l for 2 ml of emulsifier was calculated from the 15.9 mg/l contributed by 4 ml in the prior experiment shown in Table 8.

carbon content to the oil content. To allow the withdrawal of uniform aliquots for injection into the organic carbon analyzer, the oily water sample would be homogenized with the aid of an emulsifier, and the carbon content contributed by the emulsifier would be subtracted from the total organic carbon value found by analysis.

The factor that will convert the carbon content of the oil to the oil content is the ratio of the total weight of the oil to the weight of the carbon in the oil. For instance, for the hydrocarbon cetane, $C_{18}H_{38}$, this factor is the molecular weight (254) divided by the weight of 18 carbon atoms (216), which is 1.18. Cetane is a major constituent of distillate fuel, and for other hydrocarbon oils the corresponding factor would not differ substantially.

In the simplest case, where the sample consists of only oil and water, it should be necessary to determine only the total carbon content of the emulsified sample. Subtraction of the calculated carbon content contributed by a known amount of emulsifier added to the known volume of sample would give the carbon content contributed by the oil.

If the oily water sample also contains inorganic carbonates, as are present in seawater and freshwater, the inorganic carbon content also must be measured and subtracted from the measured total carbon content to obtain the organic carbon content, from which the carbon content of the emulsifier is subtracted.*

If the oily water sample also contains significant unknown amounts of dissolved non-oily organic materials, the organic carbon content of these constituents would also have to be determined and subtracted from the total organic carbon to obtain the carbon content contributed by the oil. The analysis of such samples would be more complicated. The investigation reported here essentially was directed at the ability of the method to determine oil contents and was limited to the simpler cases mentioned above.

The Beckman Model 915 Total Organic Carbon Analyzer used in the experiments was described in detail in the experimental section of this report. Samples are injected into the inorganic channel where carbonates are converted to carbon dioxide by reaction with phosphoric acid at 150°C, and duplicate samples are injected into the total channel where all carbon is converted to carbon dioxide by reaction with a cobalt oxide catalyst at 950°C. The carbon dioxide from each channel is determined with a nondispersive infrared analyzer. Comparison of the peak heights produced on a strip chart recorder with a curve of the peak heights of known standards gives the carbon contents of the samples.

Experimental Results

One problem in the evaluation of an analytical method for the determination of an oil-in-water sample is the obtaining of a known sample. Oil-in-water mixtures are not stable, and samples withdrawn from such mixtures would not remain the same. In the initial experiments,

*Alternatively, the inorganic carbon could be removed by acidifying and sparging, but this might be a complicated procedure for the oily samples.

the samples were therefore prepared in a blender, and the whole content of the blender was used as the sample. The emulsifier was first added to the water and its carbon concentration measured before the oil was added dropwise from a weighed syringe.

Various experiments were performed with Navy special fuel oil (NSFO), with Navy distillate fuel (NDF), and with white mineral oil.* Various emulsifiers were also used, including Nokomis no. 3, which is used for emulsifying oil spills at sea, and several emulsifiers supplied by Fram, Inc. for emulsifying oil with an oil test kit. Other emulsifiers used include Aerosol OT, Tergitol NPX, and the series Tergitol 15-S-3, 15-S-5, 15-S-7, and 15-S-9. The latter series consists of nonionic surfactants manufactured by Union Carbide Co., in which the solubility in water changes from very slightly soluble to very soluble as the length of a polyethylene oxide side chain is increased.

One problem encountered in the experiments with blended samples was the production of foam, which apparently was high in carbon content because it left less than the expected amount of carbon in the liquid mixture. Sampling before the foam disappeared thus gave lower carbon values attributable to the oil and lower calculated oil contents or recoveries. (The recovery is the percentage of oil found, compared to the known amount of oil added.) The recoveries were often in the vicinity of 80% for oil contents of about 10 to 100 mg/l but varied from values below 50% to occasional values approaching 150%. Examples of some results are shown in Table 1.

It was believed that the potential accuracy of the method could be better determined by intimately mixing known amounts of emulsifiers with known amounts of oil and then adding water, emulsifying the mixture, and analyzing for carbon. The emulsifier and the oil, in hexane solution, were placed into 1/2-pint, wide-mouth Mason jars, and the solvent was evaporated. The white mineral oil used for these experiments did not evaporate under the conditions used. After the addition of water, blender blades were attached to the Mason jars and the mixtures were emulsified. Mixtures containing 0, 5, and 10 mg/l of oil and selected amounts of emulsifier were prepared.

By this method, recoveries of about 70% to 95% were obtained, but occasional high apparent recoveries of up to 270% were also obtained. The latter appeared to be caused by the seepage into the mixture of grease from the blender blade bearings. An example of the results of such experiments is shown in Table 2.

To prevent contamination from the blender blade bearings, new experiments with evaporated oil and emulsifier samples were performed using an ultrasonic generator to produce the emulsions. This generator had the additional advantage of producing much less foam than the blender. To reduce the electronic noise level of the Total Organic Carbon Analyzer, the gain of the instrument was reduced and the sample was increased from 50 to 100 µl. The repeatability of the method was improved (as illustrated by the experiment shown in Table 3), but the recoveries were only about 70%. In the experiment illustrated, the carbon content contributed by

*This is also called liquid petrolatum.

the emulsifier was higher than that contributed by the oil. It was found in subsequent experiments that emulsions that were stable for 1 day could be produced with emulsifier concentrations that contributed about one-half as much carbon content as the oil contributed and that reasonably stable emulsions could be made with lower emulsifier content.

A disadvantage of the probe-type ultrasonic generator is that most of the energy is dissipated at the tip of the probe and little agitation occurs in other portions of the liquid. Thus, when dispersion of a drop of NSFO was attempted, the black oil on the glass at the surface of the liquid and also oil on the probe itself sometimes was not dispersed. Both 150- and 300-watt ultrasonic generators showed this problem. Sometimes the drop of NSFO went to the bottom of the bottle containing dilute emulsifier solution and was well-mixed. In one experiment with 10 mg/l of NSFO and 50-µl samples, 85% recoveries were obtained.

A Polytron ultrasonic generator was obtained for subsequent experiments. This mixing instrument has a high-speed impeller that provides both mechanical and ultrasonic energy. Much more agitation is provided by the Polytron than by the ultrasonic probe generators, but more foam and air entrainment are also produced. Therefore, after mixing of the sample, it was necessary to allow the entrained air to rise and to allow the foam to settle.

A variety of experiments were performed with intimate mixtures of white mineral oil and emulsifiers to develop optimum conditions of comparatively low foaming but adequate emulsification. The oil and emulsifier were measured out in Freon 113 solutions, which could be evaporated at lower temperatures than the hexane solutions. The amount of oil added gave from 0 to 20 mg/l in the 150 ml of emulsified mixture. The amount of emulsifier added was kept constant in any one experiment and was such as to provide about 5 to 15 mg/l of carbon to each sample.

The emulsifier that gave the least foam was Tergitol 15-S-5. At concentrations contributing 5 and 10 mg/l of carbon and mixed for 1 minute, the foams settled in about 1/2 and 1 hour, respectively, when no oil was present, but settled in about 7 and 30 minutes when 10 mg/l of oil was present. When no oil is present, the stirring can be greatly reduced to reduce foaming, and the carbon contributed by the emulsifier would not have to be determined for each analysis if the same concentration is always used. Tergitol 15-S-3 would probably give even less foam but is so water-insoluble that it could not be used in a practical application employing only aqueous reagents.

One experiment with 5 to 20 mg/l of white mineral oil intimately mixed with emulsifer gave average recoveries of 81% with a standard deviation of only 4.5 (as shown in Table 4). However, in other experiments, recoveries were not as reproducible; one experiment gave values of 45% to 88%. Generally, in this series of experiments, the recoveries ranged from 69% to 81%.

Ultimately the objective was the analysis of oily water, which would be performed by adding a known amount of emulsifier, emulsifying the mixture, and analyzing for organic carbon. This procedure was simulated in the next series of experiments in which a weighed drop of white mineral oil in 300 ml of demineralized water (a concentration of

about 15 mg/l) was emulsified after addition of aqueous Tergitol 15-S-5 solution. Recoveries for the white mineral oil were quite reproducible but averaged only 58% (with a standard deviation of 3).

The method was checked by replacing the white mineral oil with potassium acid phthalate, which is the chemical used to standardize the Total Organic Carbon Analyzer. By subtraction of the carbon in the emulsifier and use of the factor of 2.125 (the molecular weight divided by the total atomic weights of the carbon atoms), the recoveries for the potassium acid phthalate averaged 94%. Thus, the method appeared sound, but the white mineral oil apparently was not converted to carbon dioxide as well as the potassium acid phthalate.

It was suspected that perhaps the injection level of 100 µl might have been too high to obtain complete combustion of the oil, even though injection levels as high as 200 µl are recommended for samples low in carbon. To check this possibility, samples of emulsified white mineral oil were injected at various levels from 10 to 100 µl. As shown in Figure 3, a strong change in the slope of the curve occurs at about 35 µl, and the response per microliter is much lower at higher sample levels. For the oil and emulsifier mixture, the slope from 40 to 70 µl was only 59% of the slope from 10 to 30 µl. These results indicate that nearly one-half of the emulsified oil beyond 35 µl that was injected was not converted to carbon dioxide.

In the Beckman Model 915 Total Organic Carbon Analyzer, the sample is vaporized and combusted in a tube at 950°C. Apparently, a sample of about 35 µl of water produces sufficient steam to fill the front portion of the tube and also the portion holding the catalyst. Any additional amount injected is swept through the catalyst too rapidly to be completely oxidized. The emulsified oil is less completely oxidized under these conditions than is a potassium acid phthalate standard. For this standard solution there is also a break in the curve, but the slope from 40 to 70 µl is 86% of the slope from 10 to 30 µl. If the standard solution had shown the same reduction in response as the oil emulsion, the low recoveries at higher injection level would not have been noticed.

Subsequent experiments were performed with 25- and 35-µl samples. Although the former amount would more surely fall on the straight portion of the curve, the latter would give a higher signal-to-noise ratio and was chosen because of noise problems in the nondispersive infrared analyzer. With 35-µl samples of 15 mg/l of white mineral oil emulsified in water, an average recovery of 83% was obtained, with a standard deviation, σ, of 6.5. With 100 µl samples, the same mixture gave an average recovery of 58% (σ = 5.5). In other experiments with 25-µl samples, recoveries of 88% (σ = 8.5) were obtained, but the difference could be within experimental error.

The addition of emulsifier to obtain good samples and the subtraction of the organic carbon in the emulsifier adds an additional error. Experiments were therefore performed without emulsifier to determine whether use of the emulsifier was worthwhile. In one experiment with 15 mg/l of white mineral oil in demineralized water, recoveries of 36% to 79% were obtained (as shown in Table 6), and these values would have

been even lower if a correction had been made for carbon in the demineralized water. In another experiment with five samples, a similar increase in recoveries, from 51 to 86%, was obtained in the set of samples. It is not known whether oil was absorbed on the Polytron mixer. In other experiments with smaller numbers of samples, recoveries ranging from 71% to 93% were obtained. The reproducibilities of peak heights in multiple injections of one sample were quite poor, with standard deviations ranging from 1 to 3 units (compared to below 1 unit for emulsifed samples). Sometimes succeeding injections gave increasingly lower peaks. Lower peaks were also obtained when samples were held in the syringe for any appreciable time before being injected into the analyzer.

With 35-µl samples of 12 mg/l of Navy distillate fuel in demineralized water, a recovery of 81% (σ = 1.8) was obtained. There was a negligible difference between the recovery of the original oil and the recovery of artificially weathered oil that had lost 25% of the more volatile portion. The recovery values for weathered NDF were lower at higher concentrations, possibly because of incomplete combustion. Recovery values at different oil concentrations were as follows: 4 mg/l, 86%; 12 mg/l, 81%, 32 mg/l, 70%; 100 mg/l, 68%. Some of these results are shown in Tables 7 and 8.

In the experiments with demineralized water, the carbon impurities in the water totaled only about 1 mg/l. If only the oily water samples were available for analysis and corrections were made only for the emulsifier added, the results of the oil analyses would be expected to be too high by about 1 mg/l. But in the analyses where blanks (with emulsifier but without oil) were run, a correction was made for any carbon in the original water by subtracting not only the carbon contributed by the emulsifier but, instead, subtracting the carbon content of the aqueous solution containing the emulsifier.

In seawater the organic carbon content was about 1.7 mg/l, or only slightly higher than that of the demineralized water, but the total carbon content was about 28 mg/l because of the high inorganic carbon content contributed by the carbonates and bicarbonates in seawater. Therefore, in experiments with seawater, both total carbon and inorganic carbon were measured, and calculations were made with the difference between these values, which is the organic carbon.*

In seawater experiments with samples containing 11 and 34 mg/l of Navy distillate fuel, recoveries of 77% and 65%, respectively, were obtained when corrections were made for the organic carbon in the seawater. These results are shown in Table 9.

In a similar experiment with seawater containing 15 and 46 mg/l of white mineral oil, recoveries of 77% and 69% were obtained. These results are shown in Table 10.

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*Because the original seawater was available, calculations could have been made using only the total carbon values, but these would have been misleading because in the emulsification of the oily seawater samples, the inorganic carbon content was reduced by about 2 mg/l.

In the above experiment, the difference between the average oil contents of the two sets of samples was 31 mg/l, and the difference between the average amounts of oil found experimentally was 20 mg/l. Thus, the recovery for the additional white mineral oil added was only 65%. In the prior experiment with Navy distillate fuel, the difference in the average concentrations was 23 mg/l; and the difference in results was 14 mg/l, or a recovery of 59%. In the demineralized water experiment discussed earlier (where 12 and 32 mg/l of Navy distillate fuel gave recoveries of 81% and 70%), the difference in concentration of 20 mg/l gave a difference in results of 14.5 mg/l, or a recovery of 65%.

Significance of Results

This method of determining oil in water – by homogenizing the sample with an emulsifier that adds a known carbon content, determining the organic carbon contributed by the oil, and calculating the oil content – can be useful provided limitations of the method are kept in mind. It has been investigated as a manual method rather than an automated method.

In the experiments performed, the amounts of soluble organic materials in the water were very small and were corrected for. Under these relatively ideal conditions, and for oil contents of about 15 mg/l, the oil content found by analysis was generally near 80% to 85% of the oil content added to the samples. At oil contents of about 50 to 100 mg/l, the recoveries were about 65%.

The low recoveries could be caused by incomplete combustion of the oils. Most organic compounds are readily converted to carbon dioxide in the high temperature furnace and produce high recoveries, generally in excess of 99% (Ref 6). It appears from the experiments that oils are not as readily oxidized and, besides giving lower recoveries, may also give less reproducible results.

If the oil recoveries were always low but consistent, they would present no analytical problems. Thus, if the recoveries were always 85% using a factor of 1.18, one could use a conversion factor of 1.18 ÷ 85% – or 1.39 – to calculate the oil contents for 100% recoveries. The recoveries of 65% for samples containing about 50 mg/l of oil would then become recoveries of 76%. A higher conversion factor may be appropriate for higher concentrations of oil (for example, a factor of 1.18 ÷ 65%, or 1.82); but there were not sufficient experimental data to suggest a curve for a changing factor with changing carbon content attributable to the oil.

The reproducibilities of the recoveries for samples in a single experiment, with oil concentrations no higher than 20 mg/l, were often such that the relative standard deviations* were considerably less than 10%.

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*The relative standard deviation is the standard deviation divided by the average value; thus, for example, in Table 5, the standard deviation of 6.5 for the average recovery of 83.3% is a relative standard deviation of 7.8%.

There are many potential sources for lack of reproducibility in the operation of the Total Organic Carbon Analyzer. The specified repeatability of this apparatus, for repetitive injections of the same sample, is ±2% of full scale at 50 mg/l carbon full scale and ±5% of full scale at 10 mg/l carbon full scale.* Under good conditions, much better repeatability is possible. Thus, the standard deviations of the chart readings in the experiments with emulsified oils were generally in the range of 0.5% to 1.0% of full scale. At 40 mg/l full scale, which was a range often used, a 1% error would be 0.4 mg/l. If the error in the determination of the carbon in the emulsified sample and in the emulsifier were both 1% but in opposite directions, the total error would be 0.8 mg/l of carbon or about 1 mg/l of oil.

The errors just discussed might generally be smaller because averages of at least two readings were always taken; but, if inorganic carbon is measured and subtracted from the total carbon values, this adds to the potential errors caused by uncertainties in the chart readings. In some experiments, improper operation of the infrared analyzer added to the problems by increasing the noise levels.

The chart readings or peak heights obtained with the Total Organic Carbon Analyzer are converted to carbon contents by comparison with the peak heights produced by standard solutions. Thus, the accuracy of the measurements is no greater than the accuracy of the standard solutions. The latter can deteriorate with time. The organic standards may develop bacterial growth to give erratic readings. Inorganic carbon standards may change by several milligrams per liter in 1 week if the container is not tightly closed because the solution absorbs carbon dioxide from the air.

In addition to the errors in determination of the carbon contents, errors could occur due to retention of oil or emulsifier by the Polytron and possible transfer to other samples. The Polytron was agitated twice with water immediately after each sample mixing; and after use with oily water not containing emulsifier, it was agitated with dilute emulsifier solution and then with water. In addition to the other errors discussed, a 1% error in measurement of the water used, of the oil weighed out, or of the emulsifier added could each add a 1% error to the reproducibility between otherwise identical samples used in the experiments.

Reproducibilities of the recoveries with relative standard deviations of considerably less than 10% within a single experiment are thus as good as can be hoped for. There were not sufficient experiments performed under identical conditions to establish reproducibilities between different experiments. Under good experimental conditions, these relative standard deviations are estimated as probably not much greater than 10% where only total carbon is measured or 15% where total and inorganic carbon are measured.

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*With a Model 865 nondispersive infrared analyzer, instead of the Model 215B used in these experiments, the repeatability is improved at the lower ranges and is specified as ±5% of full scale at 5 mg/l full scale.

The precision of a method is the reproducibility and can be expressed as the relative standard deviation. The accuracy of a method is the agreement between the amount measured and the amount present and can be expressed as the percentage measured, which is the same as the recovery. Thus, the accuracy under ideal conditions was 85% for 15-mg/l oil samples and 65% for 50-mg/l samples if the theoretical factor of 1.18 was used. The average accuracies would have been 100% and 76%, respectively, if a factor of 1.39 had been used.

The accuracy of this method of determining oil in water would be reduced if interfering organic materials were present for which a correction could not be made. The demineralized water and the filtered seawater used contained about 1.5 mg/l of organic carbon. If this soluble organic carbon had not been corrected for, a positive error of about 2 mg/l of oil would have resulted. For 15 mg/l of oil, 15 mg/l would have been found instead of 13 mg/l if a factor of 1.18 were used, and 17 mg/l would have been found instead of 15 mg/l if a factor of 1.39 had been used.

When used without a correction for dissolved carbon in non-oily materials, the method thus gives only a maximum limit for the oil content rather than the actual oil content. If the estimates of the precision are correct and a factor of 1.39 is used, a sample determined to contain 9 mg/l of oil by this method could contain up to 10 mg/l of oil if no soluble organic materials were present; or it could contain lesser amounts (or even no oil at all) if sufficient soluble organic materials were present. In some cases, determination of a maximum limit for the oil content might be all that is required.

If appreciable unknown amounts of dissolved organic materials are present in the samples, these would have to be corrected for to determine the oil content. Some procedure would have to be established to measure the soluble organic carbon content and subtract it from the total organic carbon content. This problem was outside of the scope of the present investigation. However, one possible solution would be to remove insoluble oil from a duplicate sample by filtration and to determine the difference between the organic carbon contents of the unfiltered and filtered samples. If complete removal of oil by filtration were possible, the method would determine the insoluble oil in the sample rather than the total oil, but the insoluble oil is the oil that generally is most objectionable and the only oil that a separator can remove.

In a preliminary experiment, water containing 1.3 mg/l total carbon was shaken with white mineral oil equivalent to 100 mg/l. Part of the mixture was filtered through Whatman 2V filter paper, and the filtrate had a total carbon content of 5.3 mg/l. Whether this additional 4.0 mg/l represents only soluble oil or whether insoluble oil was not completely removed was not established. This approach for making a correction for all soluble organic materials and thus determining the insoluble oil in the sample may be feasible if the oil is not too well emulsified, but much more experimentation would be needed.

In the experiments described in this report, the mixing time for each sample after the addition of emulsifier was 1 minute, but this could perhaps be reduced. Sample injections must be spaced at least

2 minutes apart and three injections per sample into two channels (total and inorganic) require 12 minutes. Two injections may be sufficient if the values agree, but a sample injection may at times produce a peak that differs so much from the average that it needs to be rejected. In some cases the inorganic carbon content may be known, and these determinations can be omitted. The average working time per sample, including cleaning of the emulsifying apparatus, may thus be 15 minutes. The average elapsed time, including settling of foam and calculation of results, may be 25 to 30 minutes for any one sample. These time requirements can be reduced if the foam settles rapidly and if the number of injections can be reduced.

The method of determining oil in water by emulsification and carbon analysis could be a useful manual method, where the dissolved organic carbon content is known or will not limit the usefulness of the results and where personnel skilled in the use of the carbon analyzer are available. The accuracy and precision of the method would need to be further established, particularly for seawater samples or other water samples of high inorganic carbon content. Where there is substantial unknown dissolved organic carbon present, a method of correcting for this would have to be devised.

As mentioned earlier, the results were obtained under relatively ideal conditions. More work would have to be done to determine to what extent this method would be a useful laboratory technique. For example, samples were run in order of increasing oil content, and the possible carryover of oil from a sample of high oil content to a sample of low oil content by the Polytron mixer has not been determined. The Polytron mixer will retain some oil when oil is homogenized without emulsifier; and when the Polytron mixer is cleaned with relatively concentrated emulsifier solutions, considerable rinsing is necessary to remove residual emulsifier.

More extensive experimentation would be necessary to determine whether the estimated reproducibilities between experiments, as cited earlier, can be maintained. It was not always possible to reproduce experiments that well — sometimes because of known experimental difficulties and sometimes for unknown reasons. The unknown reasons might have included the operation of the Total Organic Carbon Analyzer. The precision or reproducibility of this analyzer is given as a standard deviation of about 1 to 2 mg/l (Ref 1, p. 534) and as a standard deviation of about 4 mg/l (Ref 7), and both of these are much greater standard deviations than observed in most of the experiments presented in the tables of this report. Some of the analytical errors are probably associated with deterioration of standards, and better methods of handling these (other than refrigeration in glass-stoppered bottles between use) would be desirable.

Direct comparison with the extraction-infrared spectroscopy method, with respect to accuracy and time required, would be desirable before employing the organic carbon method as a manual method for oil-in-water determinations. Finally, sampling methods would have to be evaluated. However, no further work is planned.

CONCLUSIONS

1. Total organic carbon analysis can be useful as a manual method for the determination of oil in water, provided the limitations of the method are taken into account.

2. The use of an emulsifier to provide a more homogeneous mixture of the oil and water, and subsequent correction for the carbon added, gives more reproducible analytical results than analysis without the emulsifier.

3. Under ideal laboratory conditions, oil of up to 15 mg/l (or ppm) was analyzed with recoveries of about 85% and relative standard deviations below 10%.

4. At oil contents of about 50 mg/l, the recoveries were about 65%.

5. The oil apparently was not completely combusted to carbon dioxide in the Beckman Total Organic Carbon Analyzer. Therefore, the theoretical conversion factor of 1.18 from carbon found in the oil to oil present might be too low. A value of 1.39 would, on the average, have given the theoretical amount of oil for 15-mg/l samples and 76% recoveries for 50-mg/l samples.

6. Organic carbon contributed by non-oily material will give high results and must be corrected for. If no corrections are made, the method will give only an upper limit for the oil content.

7. The analysis of a filtered sample may be suitable as a method of correcting for dissolved organic materials.

8. The method investigated is non-automated and requires reasonable laboratory skill.

9. After the instrument is standardized, an estimated working time of 15 minutes is required per sample, and the elapsed time is about 25 minutes for an average sample. (The time requirements could be reduced under some circumstances.)

10. Although comparatively good accuracy and precision are possible under ideal conditions, as noted earlier, further study of the method under anticipated conditions of use would be desirable before using the method as an analytical procedure.

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Figure 1. Total Organic Carbon Analyzer.

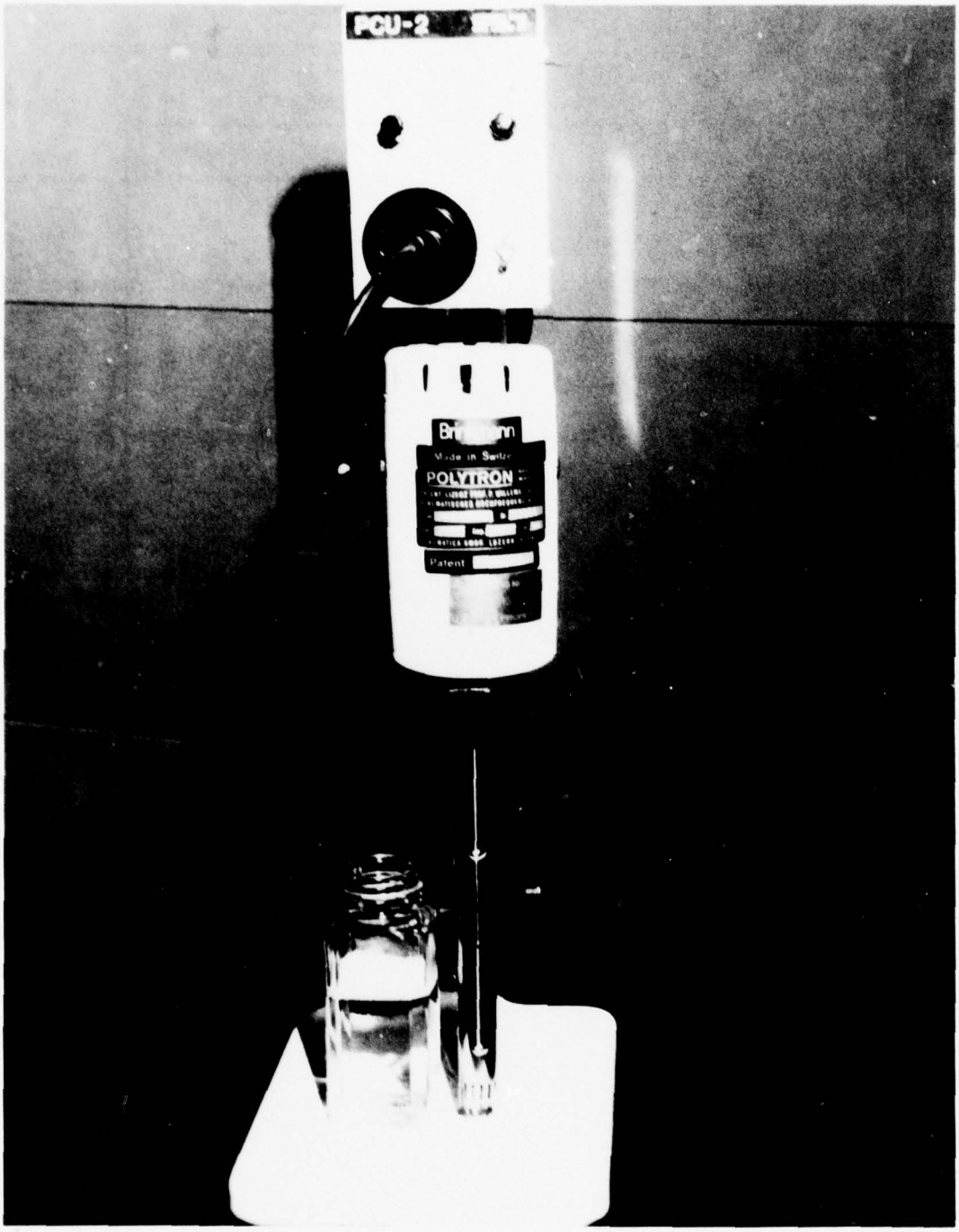

Figure 2. Polytron Homogenizer.

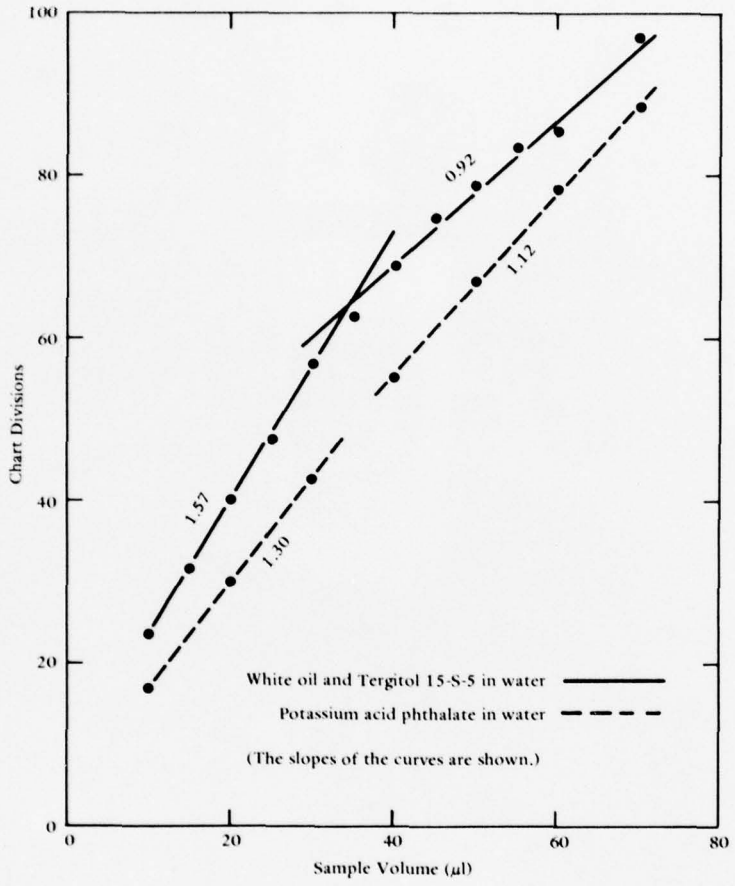

Figure 3. Effect of sample volume on instrument response.

Table 1. Analysis of White Mineral Oil Emulsified in Open Blender

White Mineral Oil Added[a]		Total Carbon[b] (mg/l)	Carbon in Oil[c] (mg/l)	Oil Content[d] (mg/l)	Recovery[e] (%)
(mg)	(mg/l)				
none	none	25	none		
4.0	8.0	34	9	10.6	133
8.2	16.4	45.5	20.5	24.2	148
16.4	32.8	59	34	40.1	122

[a]Added to 500-ml demineralized water containing 2 ml of aqueous 1% Aerosol OT.

[b]Obtained by conversion of average peak height to carbon content.

[c]Previous column entry less 25 mg/l contributed by emulsifier and water.

[d]Previous column entry multiplied by 1.18.

[e]Previous column entry divided by the known white mineral oil content (second column).

Table 2. Analysis of White Mineral Oil-Emulsifier Mixture in Closed Blender

White Mineral Oil (mg/l)	Peak Height[a] (units)	Total Carbon (mg/l)	Carbon in Oil[b] (mg/l)	Oil Content[c] (mg/l)	Recovery (%)
none	44	16.3	none		
none	48.5	18.1	none		
5	56.5	21.2	4.0	4.7	94
5	73.5	28.5	11.3	13.3	267
10	60.5	23.0	5.8	6.8	68
10	60	22.7	5.5	6.5	65

[a] 50 µl of 40 mg/l standard gave a peak height of 90.5 units.

[b] Previous column entry less 17.2 mg/l contributed by Tergitol 15-S-5 and water.

[c] Previous column entry multiplied by 1.18.

Table 3. Analysis of White Mineral Oil-Emulsifier Mixture Using Sonic Dismembrator 300

White Mineral Oil (mg/l)	Peak Height[a] (units)	Total Carbon (mg/l)	Carbon in Oil[b] (mg/l)	Oil Content[c] (mg/l)	Recovery[d] (%)
none	49.7	18.4	none		
none	50.2	18.7	none		
none	50.9	18.9	none		
5	56.8	21.3	2.6	3.0	60
5	57.8	21.6	2.9	3.4	68
5	56.4	21.2	2.5	3.0	60
10	64.9	24.8	6.1	7.2	72
10	64.3	24.5	5.8	6.8	68
10	64.1	24.4	5.7	6.7	67
15	72.6	28.2	9.5	11.2	75
15	73.5	28.6	9.9	11.7	78
15	71.9	27.8	9.1	10.7	70

[a] 100 µl of 40 mg/l standard gave a peak height of 100 units.

[b] Previous column entry less 18.7 mg/l contributed by Tergitol 15-S-5 and water.

[c] Previous column entry multiplied by 1.18.

[d] Average recovery is 68.7% with a standard deviation of 6.1.

Table 4. Analysis of White Mineral Oil-Emulsifier Mixture Using Polytron Homogenizer

White Mineral Oil (mg/l)	Foam Settling Time (min)	Turbidity (JTU[a])	Peak Height[b] (units)	Total Carbon (mg/l)	Carbon in Oil[c] (mg/l)	Oil Content[d] (mg/l)	Recovery[e] (%)
none	35	0.35	14.6	5.0	none		
none	33	0.30	15.1	5.3	none		
5	13	8.1	22.6	8.2	3.1	3.7	73
5	12	8.2	23.4	8.5	3.4	4.0	80
10	6	32	31.2	11.6	6.5	7.7	77
10	8	33	32.3	11.9	6.8	8.0	80
15	10	58	42.4	16.1	11.0	13.0	86
15	8	62	41.6	15.7	10.6	12.5	83
20	7	78	51.6	19.7	14.6	17.2	86
20	6	78	50.7	19.3	14.2	16.8	84

[a]Jackson turbidity units.

[b]100 µl of 20 mg/l standard gave a peak height of 52.2 units.

[c]Previous column entry less 5.1 mg/l contributed by Tergitol 15-S-5 and water.

[d]Previous column entry multiplied by 1.18.

[e]Average recovery is 81.1% with a standard deviation of 4.5.

Table 5. Analysis of White Mineral Oil in Water

White Mineral Oil Added[a]		Peak Height		Total Carbon (mg/l)	Carbon in Oil[d] (mg/l)	Oil Content[e] (mg/l)	Recovery[f] (%)
(mg)	(mg/l)	(units[b])	(σ[c])				
none	none	21.0	0.3	8.5	none		
none	none	20.8	0.3	8.4	none		
none	none	20.3	0.3	8.2	none		
4.3	14.3	42.4	0.9	18.2	9.8	11.6	81
4.3	14.3	41.8	0.4	17.8	9.4	11.1	77
4.0	13.3	40.3	0.6	17.2	8.8	10.4	78
4.25	14.2	45.1	0.6	19.3	10.9	12.9	91
4.1	13.7	44.0	1.0	18.8	10.4	12.3	90

[a]White mineral oil added to 300 ml of demineralized water, followed by 2 ml of aqueous Tergitol 15-S-5 calculated to contain 1,500 mg/l of carbon, emulsified with Polytron.

[b]35 µl of 20 mg/l standard gave a peak height of 46.9 units.

[c]Standard deviation for three injections of non-oily samples or for five injections of oily samples.

[d]Previous column entry less 8.4 mg/l average of samples without oil.

[e]Previous column entry multiplied by 1.18.

[f]Average recovery is 83.3% with a standard deviation of 6.5.

Table 6. Analysis of White Mineral Oil in Water Without Emulsifier

White Mineral Oil Added[a]		Peak Height		Total Carbon (mg/l)	Oil Content[d] (mg/l)	Recovery[e] (%)
(mg)	(mg/l)	(units[b])	(σ[c])			
4.4	14.7	12.4	1.7	4.5	5.3	36
4.25	14.2	16.4	2.7	6.3	7.4	52
4.3	14.3	17.9	2.8	6.9	8.1	57
4.4	14.7	22.2	1.3	8.9	10.5	71
4.35	14.5	23.8	1.8	9.7	11.4	79

[a]Added to 300 ml of demineralized water; homogenized with Polytron without addition of emulsifier.

[b]35 µl of 10 mg/l standard gave a peak height of 24.6 units.

[c]Standard deviation for five injections.

[d]Previous column entry multiplied by 1.18.

[e]Average recovery is 59% with a standard deviation of 17.

Table 7. Analysis of Navy Distillate Fuel in Water (Weathered and Unweathered)

NDF Added[a,b]		Peak Height		Total Carbon (mg/l)	Carbon in Oil[e] (mg/l)	Oil Content[f] (mg/l)	Recovery (%)
(mg)	(mg/l)	(units[c])	(σ[d])				
none	none	20.8	0.4	7.9	none		
none	none	21.1	0.2	8.1	none		
3.3	11.0	37.5	0.2	15.7	7.7	9.1	83
3.7	12.3	38.5	1.0	16.2	8.2	9.7	78
3.4	11.3	37.7	1.1	15.8	7.8	9.2	81
3.5	11.7	37.8	0.5	15.9	7.9	9.3	80
9.3	31.0	60.2	0.4	26.4	18.4	21.7	70
10.0	33.3	62.1	0.7	27.3	19.3	22.8	68
10.6	35.3	68.2	0.9	30.1	22.1	26.1	74
10.55	35.2	65.3	1.0	28.8	20.8	24.5	70
	11.6[g]					9.3[g]	81
	33.7[g]					23.8[g]	70
	22.1[h]					14.5[h]	65

[a]Added to 300 ml of water, followed by 2 ml of aqueous Tergitol 15-S-5 calculated to contain 1,500 mg/l of carbon, emulsified with Polytron.

[b]For each set of four oily samples, the first two contain unweathered NDF and the last two contain weathered NDF.

[c]35 µl of 30 mg/l standard gave a peak height of 67.8 units.

[d]Standard deviation for three injections.

[e]Previous column entry less 8.0 mg/l contributed by emulsifier.

[f]Previous column entry multiplied by 1.18.

[g]Average of four above samples.

[h]Difference between the two averages.

Table 8. Analysis of Navy Distillate Fuel in Water (Weathered Only)

NDF Added[a]		Tergitol[b] (ml)	Peak Height		Total Carbon (mg/l)	Carbon in Oil (mg/l)	Oil Content[e] (mg/l)	Recovery (%)
(mg)	(mg/l)		(units[c])	(σ[d])				
none	none	none	1.7	0.2	1.4	none		
none	none	2	10.7	0.4	9.2	none		
none	none	4	19.2	0.2	17.3	none		
9.2	30.7	2	29.9	0.4	27.9	18.7[f]	22.1	72
9.4	31.3	4	36.5	0.9	34.7	17.4[g]	20.5	66
18.9	63.0	2	48.5	1.2	47.5	38.3[f]	45.2	72
18.9	63.0	4	52.9	0.8	52.4	35.1[g]	41.4	66
30.9	103	4	72.4	1.9	74.8	57.5[g]	67.9	66
31.9	106.3	2	70.3	1.7	72.2	63.0[f]	74.3	70

[a]Weathered Navy Distillate Fuel added to 300 ml of demineralized water.

[b]Aqueous Tergitol 15-S-5 calculated to contain 1,500 mg/l of carbon.

[c]35 µl of 100 mg/l standard gave a peak height of 92.2 units.

[d]Standard deviation for five injections.

[e]Previous column entry multiplied by 1.18.

[f]Previous column entry less 9.2 mg/l contributed by emulsifier.

[g]Previous column entry less 17.3 mg/l contributed by emulsifier.

Table 9. Analysis of Navy Distillate Fuel in Seawater

NDF[a] (mg/l)	Total Carbon		Inorganic Carbon		Organic Carbon[d] (mg/l)	Carbon in Oil[e] (mg/l)	Oil Content[f] (mg/l)	Recovery[g] (%)
	Peak Height[b] (units)	Content (mg/l)	Peak Height[c] (units)	Content (mg/l)				
none[h]	48.9	29.0	45.6	27.1	1.9	none		
none[h]	48.8	28.9	45.7	27.1	1.8	none		
11.7	67.1	41.9	41.8	24.9	17.0	7.2	8.5	73
10.5	67.1	41.9			17.0	7.2	8.5	81
11.3	67.4	42.0			17.1	7.3	8.6	76
34.5	85.2	53.6	42.2	25.1	28.5	18.7	22.1	64
34.0	85.2	53.6			28.5	18.7	22.1	65
34.2	85.3	53.7			28.6	18.8	22.2	65

[a]Weathered Navy Distillate Fuel added to 300 ml of seawater, followed by 2 ml of aqueous Tergitol 15-S-5 calculated to contain 1,500 mg/l of carbon, emulsified with Polytron.

[b]35 µl of 60.8 mg/l standard gave a peak height of 95.0 units; standard deviations for three injections 1.0 or less.

[c]35 µl of 40.3 mg/l standard gave a peak height of 67.4 units; standard deviations for three injections 0.6 or less.

[d]Total carbon less inorganic carbon.

[e]Previous column entry less 9.8; 1.85 for organic carbon in seawater plus 7.95 for organic carbon in Tergitol based on prior experiment.

[f]Previous column entry multiplied by 1.18.

[g]Average recovery for 11 mg/l samples is 77%; average for 34 mg/l samples is 65%.

[h]No oil or emulsifier added.

Table 10. Analysis of White Mineral Oil in Seawater

White Mineral Oil[a] (mg/l)	Total Carbon		Inorganic Carbon		Organic Carbon[d] (mg/l)	Carbon in Oil[e] (mg/l)	Oil Content[f] (mg/l)	Recovery[g] (%)
	Peak Height[b] (units)	Content (mg/l)	Peak Height[c] (units)	Content (mg/l)				
none[h]	48.9	27.4	46.1	25.8	1.6	none		
none[i]	58.9	33.7	42.9	23.7	10.0	none		
15.0	73.0	43.0	42.0	23.1	19.9	9.9	11.7	78
15.2	73.6	43.4			20.3	10.3	12.2	80
14.0	71.3	41.8			18.7	8.7	10.3	73
46.8	98.1	59.9	42.1	23.2	36.7	26.7	31.5	67
46.5	100.2	61.2			38.0	28.0	33.0	71
45.8	97.5	59.5			36.3	26.3	31.0	68

[a]White mineral oil added to 300 ml of seawater, followed by 2 ml of aqueous Tergitol 15-S-5 calculated to contain 1,500 mg/l of carbon, emulsified with Polytron.

[b]35 µl of 60.8 mg/l standard gave a peak height of 99.7 units; standard deviations for three injections of each sample were 0.8 or less.

[c]Used same standardization curve as for total carbon; standard deviations 0.6 or less.

[d]Total carbon less inorganic carbon.

[e]Previous column entry less 10.0 for seawater plus Tergitol.

[f]Previous column entry multiplied by 1.18.

[g]Average recovery for 15 mg/l samples is 77%; average for 46 mg/l samples is 69%.

[h]Seawater without oil or Tergitol.

[i]Seawater without oil but with Tergitol.

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