Now - with the advent of a fluorometer specifically designed for field service - the highly specific fluorescence of the aromatic components of oil may be used to:

- **MEASURE BOTH EMULSIFIED AND DISSOLVED OIL IN WATER**
- **PERFORM BASELINE STUDIES ON OIL IN WATER**
- **PINPOINT UNDERSEA OIL LEAKS AND NATURAL SEEPS**
- **MEASURE OIL IN ORGANISMS, SEDIMENT AND AIR**

Crude and most refined petroleum products contain large amounts of aromatic hydrocarbons. Eight different crude and refined oils, for example, contained from a low of 12.1% to a high of 46.6% aromatics (1).

Products of recent biological activity rarely contain aromatics (2, 3, 4).

Aromatics may be distinguished from products of recent biological activity since those associated with oil are highly fluorescent at relatively short wave lengths. This fluorescence may be measured both in oil-accommodated water and in solvents used to extract oil from water, sediment and organisms (3, 5, 6, 7, 8).

The limit of detectability of oil in sea water, on a continuous-flow basis with no sample treatment whatever, has been reported at five parts per billion (PPB) (9). Extractive techniques may be used on individual samples. Limits of detectability of 0.2 PPB (10) and 1 PPB (6) have been reported.

Instruments are available for lab or boat operation (11). (See EQUIPMENT RECOMMENDATIONS, TURNER DESIGNS, below.)

The same equipment used to measure oil may also be used for turbidity measurements (12, 13), determination of suspended solids (14), dye tracer studies (15, 16, 17), flow measurements (18, 19) and measurement of algae and chlorophyll (20).

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AN OVERVIEW

The Turner Designs fluorometer can provide on-site measurement and tracking of polynuclear aromatic hydrocarbons (PNAs) (carcinogens) heading for water supplies or shellfish beds. It will also save time and money in Gas Chromatographic (GC) analysis.

The fluorometer gives instant, on-site measurement of relative concentrations of PNAs, which are carried by the current, are invisible and may well be a problem long after the unsightly slick has dispersed.

A fluorometer will not, however, measure the visible material on the surface, totally replace GC analysis or do well on gasoline (there are few PNAs).

If there is no fluorescence, there cannot be any PNAs. The fact that there is fluorescence does not prove that there are PNAs. Fluorescence of a random sample from some arbitrary body of water has little meaning. If you are tracking an oil spill, however, it is a good bet that fluorescence means the presence of PNAs. While you are confirming this with GC analysis of a few samples, you are justified in warning water supplies or in taking other action.

River Spills

Long after the visible slick (the stuff that makes the newspapers) had gone in the Ashland Oil Spill of 1987, there was actually a potentially more serious problem being faced. The PNAs from the diesel fuel had dissolved in the water and were heading downstream. The various municipal water supplies downstream certainly did not wish to take carcinogens into their system. On the other hand, few communities had enough storage capacity to permit shutting down for longer than absolutely necessary.

Since dissolved carcinogens are not visible, a chemical or instrumental means of detection was required. The widely recognized GC analysis, though definitive, was slow and expensive. To track the progress by this means would have been virtually impossible because it would have required collecting and labeling thousands of individual samples. Time was also a factor. Analyzing these samples on a meaningful time scale would have required a staggering number of chemists, each with expensive equipment.

Because PNAs fluoresce, several agencies tracked the plume with Turner Designs Model 10 Fluorometers. These had the advantages, they found, of being rugged, portable and battery operable instruments giving instant, on-the-spot answers with no chemical manipulation.

One agency rigged a Pitot tube intake at the bow of its boat, taking water in continuously, running it through the fluorometer and recording the answer. The analysis took place at 35 knots. Considering that the plume was at one point 50 (or more) miles in length, the fact that it could be mapped in about one and a half hours was a lifesaver.

Dispersed Spills

When a dispersant is used, the response team is commonly required to track the dispersed spill. Again, the specified analysis is gas chromatographic, but even in the early stages there can be a serious problem deciding where to collect samples to send to the laboratory. At night, or in rough weather, even the main portion may not be visible.

At least one response team currently has a Model 10 Fluorometer aboard the response vessel to use as the principal means of mapping. When the Model 10 Fluorometer is used, only meaningful samples need be analyzed.

Lake Spills

Some years ago, in winter, a spill of some 6,000 gallons of fuel oil occurred in Lake Champlain. Oil was coming into Burlington's water supply. The question was if any of the water intakes were usable.

A local consulting firm had a Turner Designs fluorometer. With one phone call, a short-wavelength oil kit was put on a plane to the firm. Testing revealed that none of the intakes were usable, but there was (surprisingly) no oil between the water intakes and the spill. There was oil on the other side of the intakes.

The surprise plume was tracked by chopping holes in the ice and sliding the fluorometer to each hole on a sled. It seems that there was an unreported spill of some 8,000 gallons of diesel fuel some distance up in a little creek feeding into the lake. In this case, the fluorometer did a job it wasn't initially brought in to do.

Ocean Spills

As in river spills, the visible slick may not be the only problem. In comparison with rivers, where it is known what direction the current is, the ocean is less known. If the PNAs drift over shellfish beds, the beds should be quarantined for a time. For many years, Turner Designs fluorometers have been used to track the PNAs when shellfish beds were at risk.

Writer's Note

Fluorescence does not totally replace GC analysis, but it does save time, money and tempers. Those who have tried it will not be without it.

THE GOOD NEWS!

Continuous, real-time surveys for oil in the water column may be made at any speed at which a boat-mounted probe can be pulled through the water.

Baseline or blank fluorescence of various bodies of water is typically in the order of 100 parts per billion (PPB) in clear ocean water and 250 PPB in the shipping channel in South San Francisco Bay.

The baseline fluorescence is amazingly uniform. When oil is introduced into otherwise clean ocean water, a change of as little as 2 PPB may be detected. In the South San Francisco Bay, changes of 10 PPB were clearly evident.

Oil in the water column does not spread as surface slicks do. In tests in the South San Francisco Bay, “step” changes of 10 to 20 PPB were repeatedly traversed in distances as short as ten yards. The ability to rapidly locate such changes makes it easy to follow oil precisely to its source.

The equipment is simple, rugged and portable. In the South San Francisco Bay tests, a 12-foot boat and two fluorometers were used. One was set up to be sensitive to naphthalenic fractions present in all oils, while the second was set up to be sensitive to heavy crude, but not to lighter oils.

All equipment was loaded in a station wagon equipped with a car-top boat rack, by one person. All operations in the boat were easily carried out by one person. A single automotive storage battery was used to power all equipment. It had sufficient capacity to run the two fluorometers, the six-gallon-per-minute sample pump and a two-channel recorder for about seven hours without recharge.

The tests were run at about three knots. Addition of a spray shield at the point where the sample probe enters the water should allow tests to be run at up to ten knots.

THE BAD NEWS!

Oils are basically extremely complex mixtures of compounds with wide variations in physical and chemical characteristics.

When oil enters the environment, this mixture of compounds partitions and weathers in a very complex manner.

This makes the preparation of standards and the interpretations of data a complex matter. See the sections entitled STANDARDS and MEASUREMENT, below, for a more complete discussion.

OIL SPILLS

The public and the press identify oil spills with the immediate and highly visible oil slick, and with oil that eventually reaches and pollutes the beach. This is, in fact, only part of what happens.

An excellent discussion of what occurs, with a very complete bibliography, is available (21, pp 43-72). A review of the 35 largest oil spills since 1942, with 52 references, has been made (21A).

Initial surface-tension spreading is amazingly rapid. Expect a 100-cubic-meter (100-ton) spill of crude in the ocean to have an average thickness of .055 cm (.022 inch) in seventeen minutes, and the slick at that time to have a maximum dimension of 0.34 km (0.21 mile).

Evaporation is rapid. About half the oil will enter the atmosphere within ten days, and little returns to the water.

The relatively water-soluble and toxic aromatic hydrocarbons enter the water column directly.

The weathered surface film eventually becomes a semisolid mass and bunches up into relatively

thick patches under the influence of wind and waves.
This remaining surface oil, now quite heavy because of loss of volatile material, is emulsified by turbulence and enters the water column. Many of these emulsified particles eventually adhere to suspended solids, are consumed by zooplankton and incorporated into fecal pellets, etc. and find their way to the bottom (22, 23).

Fluorometry is particularly useful in following oil in the water column. This is important, since the subsurface plume may go in quite a different direction from the wind-driven surface slick (9, 24).

For most work, the fluorometer will be made sensitive to the naphthalenic compounds, by proper choice of excitation and emission wavelengths (see EQUIPMENT RECOMMENDATIONS, TURNER DESIGNS, below).

When set up to measure naphthalenic compounds, the fluorometer responds to both truly dissolved naphthalenes and to naphthalenes present in the emulsion phase. Caution should be used, however, since naphthalene is soluble to between 20 parts per million (PPM) (8, 28) and 30 PPM (21, p 47), well beyond the linear range of fluorescence measurement. Similar caution is required where high concentrations of emulsified oils are present. Our tests with #2 fuel oil show deviations from linearity of 2 PPM and that measurements are useful with a calibration curve to about 10 PPM.

Where crude oil is involved and where the oil is present as an emulsion, excitation and emission at longer wavelengths (350 and 410 to 550 nm) may be used. Our tests on emulsified Prudhoe Bay crude showed a linear relationship between fluorescence and oil concentration to 50 PPM. A calibration curve could be used to about 200 PPM. (See EQUIPMENT RECOMMENDATIONS, TURNER DESIGNS, below.)

A continuous-flow submersible fluorometer has been used to study the impact of the subsurface plume of soluble and emulsified hydrocarbons (25). The equipment has been described (9). It may be used to a depth of 100 meters (330 ft).

BASELINE, SEEPS AND LEAKS

The ocean, well away from spills, leaks and natural seeps, is extremely low in oil. An excellent review of sources of oil in the ocean, including maps of submarine seeps throughout the world, is available (23).

Fluorometric measurements have been used to determine the very low levels of oil present in the open ocean. For studies in such pristine environments, solvent extraction of water samples to concentrate the oil prior to measurement has been widely used (6, 10, 26, 27, 28).

Fluorometric measurements have been used to establish baselines where oil in water was expected. This is extremely important when new installations or operations involving oil are contemplated. A towed, submersible fluorometer was used to explore the proposed site for the Louisiana Offshore Oil Port (LOOP) (9, 29). Oil concentrations ranged between 30 and 300 PPB. Five traverses each about five miles long were carried out in about nine hours. The Environmental Devices Corporation towed underwater fluorometer system was deployed from the Coast Guard cutter Acushnet. Towing depth was 1.9 meters for one survey and 4.0 meters for the second survey. For such depths, it would be far less expensive and more convenient to leave the fluorometer on board and tow a pump. ENDECO will mount a pump in a controllable fish.

The same towed system was used to explore natural oil seeps off Santa Barbara (9). The Santa Barbara tests, sponsored by NOAA's Spilled Oil Research Team, was successfully carried out from a 22-foot boat, in four-foot seas.

Fluorometric measurements have the potential of rapidly pinpointing the precise source of oil leaks and seeps. As mentioned in THE GOOD NEWS!, above, we found sharp changes in the amount of oil present in the water column, in amazingly short distances. Sharp changes in oil concentration could be located to within ten yards while cruising at three knots.

Oil in the water column does not spread out the way a surface slick does. Presumably, the interface between water that contains oil and water that does not contain oil could be rapidly followed to its source.

OIL IN SEDIMENT

The determination of oil in sediment is important, since most of the heavy fractions of oil that enter the ocean eventually end up on the bottom or the beach. (See OIL SPILLS, above.) Fluorometry is particularly advantageous for measurement of oil in sediments, since interference from materials of recent biogenic activity is minimal and since the aromatics measured by fluorescence are the most toxic and longest-lived fraction of oil.

It is necessary to choose emission wavelengths so that the fluorescences of chlorophyll, pheophytin and other pigments do not interfere (28). The fluorescence of humic material cannot be avoided (30). Spectral curves of various materials obtained from freshwater sources and from sediments rich in organic materials carried by fresh water are available (30). Interferences may be expected from aromatic hydrocarbons believed to have originated in brush and forest fires (31).

Perhaps one of the most completely studied oil spills to date was caused by the stranding of the Arrow in February 1970, on the shore of Chedabucto Bay, Nova Scotia. In a recent study of residual oil in beach sand, the n-alkanes were shown to be degraded while the fluorescent aromatics were not. Fluorescent spectra of samples of the original oil were compared with spectra of oil from stranded tar layers and subsurface sediments. The shapes of the spectra of the oil from the subsurface sediments were identical with the original oil, indicating that the aromatics were not selectively degraded (32).

Detailed procedures for extraction are available (2, 32, 33, 34, 35, 36, 37). Sample storage and preservation are discussed (2, 33, 36).

OIL IN ORGANISMS

The determination of the fluorescent aromatic fractions of oil in organisms is important, since many organisms can concentrate these relatively toxic materials. A fish (Fundulus heteroclitus) is reported to concentrate aromatics by factors as large as 2700 (38). Coho salmon concentrate various aromatics by factors of 12 to 90 (39). The annelid Neanthus arenaceodentata concentrates naphthalenes by a factor of ten (40). Reference 40 contains an extensive bibliography of other uptake studies.

Details of collection, sample preparation, sample preservation and extraction are discussed (4, 32, 34, 35, 41).

Zitco (42) discusses a simple method for gross measurement of aromatics in organisms, using a spectrofluorometer. A filter fluorometer may also be used.

OIL IN AIR

Fluorometry has been used to determine the quantity of oil in air (43). This detailed procedure was developed to determine the amount of oil mist in the output of air compressors but can be easily extended to any situation where an oil mist is present.

OIL ON THE LAND

Oil spills on the land may pollute groundwater for hundreds of years. Methods of transport, laboratory percolation experiments and persistence are discussed (44). Twenty five references are cited.

EXTRACTION

This discussion is limited to extraction of oil from water, since extraction of oil from sediment and from organisms has been discussed in the sections entitled OIL IN SEDIMENT and OIL IN ORGANISMS, above.

Extraction of oil from water is called for when it is necessary to measure oil below about 2 PPB, or where various forms of analysis other than fluorescence measurements will be used.

Problems encountered in sampling and extraction are discussed (27). Details of cleaning sample bottles are given. Methylene chloride was used in preference to carbon tetrachloride because it boils at a lower temperature (40.1^{o} C vs. 76.8^{o} C) and yields a higher recovery of volatile fluorescent fractions when evaporating. Extracts, in particular those in methylene chloride, must be kept in the dark. Extraction with heavy materials, such as methylene chloride and carbon tetrachloride, is far easier to perform in the field than extraction with materials that are lighter than water, such as hexane and pentane (6). Methylene chloride yielded much better

recoveries than carbon tetrachloride (90% vs. 48%). Methylene chloride has the additional advantage that the extract need not be evaporated to dryness. Fluorescence measurements may be made directly on methylene chloride extracts. This is not the case with carbon tetrachloride extracts, since carbon tetrachloride quenches the fluorescence of oil. Methylene chloride is, however, highly volatile, which makes it difficult to store samples and to prepare standards.

Freon 113 (2, 2, 3 - trichlorotrifluoroethane) has been used as an extractant because of its low toxicity (45).

Reagents must be very carefully evaluated for fluorescent impurities. Great differences exist between reagents from different suppliers (66).

A submersible solvent extraction device has been described (46). The solvent used was hexane, which does not quench fluorescence. A logical extension of this device would be a continuous-flow extraction device which would act as a continuous-flow concentrator. The hexane extract could go directly to a continuous-flow fluorometer.

Where samples must be preserved for later extraction, the addition of 20 milligrams of mercuric chloride per liter and freezing has been used (10). It is very likely that this step could be eliminated where only fluorescence measurements will be made, since the aromatics are far less biodegradable than the other constituents of oil.

STANDARDS

Perhaps the most difficult problems in the measurement of oil in the environment are:

1. What standard should be used?

2. How should the standard be treated?

3. What accuracy is available and acceptable?

These problems exist because oil is a complex mixture of compounds that pass through many partitioning steps before a sample is taken. These include:

1. Loss of light hydrocarbons to the atmosphere.

2. Selective entry of hydrocarbons into the water column, depending on their solubility.

3. Selective entry of emulsified oil into the water column as a function of wave action and the presence of materials in the water that act as emulsifiers (47, 48, 49).
4. Removal of emulsified oil from the water column by contact with heavy particulate material.
5. Selective uptake in organisms.

6. Selective biodegradation.

7. Selective chemical reaction.

8. Selective destruction by sunlight.

If all that is needed is to be able to correlate the readings of several fluorometers (as was the case with people plotting the aromatic plume from the Ashland oil spill), a solution of naphthalene in water is convenient. A useful concentration is 0.1 PPM.

Occasionally, the problem is simple. For example, in the study of oil mist in compressed air (43), the only source of oil was the compressor, and all of the above processes were minimal. The compressor oil was an adequate standard. Again, in attempts to locate the source of an ongoing leak or natural seep, the location of a measurable discontinuity is the important thing. An absolute standard is not required.

Usually, the problem is not simple.

For baseline or deep ocean surveys, an educated guess must be made, since there is no explicit knowledge of the source of the original oil. Cretney and Wong (10) followed a typical Bunker C oil through their analysis procedure, then determined its concentration in terms of the fluorescence of chrysene. Oil in water was henceforth referenced in terms of chrysene equivalents.

Where possible, standards should be subjected to weathering tests to approximate the weathering that the unknown has received.

Thruston and Knight (50) found only minor changes in the fluorescence characteristics of four relatively dark crude oils in a four-day sunlight test. A deep amber South Louisiana crude showed a major drop in fluorescence emission, but little change in the shape of the emission spectrum. The samples studied were

recovered from the surface of the water used in the weathering test.

Frank (5, 51, 52) reports only minor variation in intensity and little variation in relative fluorescence with aging of oil films.

Artificial aging studies in large tanks with sediment on the bottom have been made (22). These tests are probably more similar to actual weathering than the small-scale tests of Frank. They do not, however, include wave action, believed important to emulsion formation. Surface film, oil in the water column and oil in the sediment layer were followed for 101 days. Major changes in fluorescence characteristics did occur during this period.

The importance of emulsion vs. gentle dissolution of the water-soluble oil fractions is clearly shown by Hornig (28). Nigerian crude oil, emulsified in water, showed a broad fluorescence emission peak centered at 470 nm and a broad excitation peak centered at 340 nm. When gently dissolved in the water, the Nigerian crude oil showed a narrow fluorescence emission peak centered at 335 nm and a narrow excitation peak centered at 285 nm. A #2 fuel oil, expected to be relatively free of polynuclear aromatics but to contain benzene and naphthalene, behaved very differently. The fluorescence spectra obtained with emulsified oil and with gently dissolved oil were nearly identical. They were also nearly identical to the spectra of the gently dissolved Nigerian crude and to the spectra of naphthalene dissolved in methylcyclohexane.

Relatively stable emulsions of oil in water can be made using ultrasonification (53, 54). These emulsions can be easily diluted. Both papers report that there was no substantive change in the chromatographic or spectral qualities of oil recovered from the emulsion, as compared with the initial oil.

A general reference on the factors affecting formation of emulsions with probe-type sonicators was published recently (55).

The stability of a standard should be checked under the precise measurement conditions that will be used in practice. Hand-shaken emulsions of Empire crude, Louisiana light crude and #2 fuel oil were prepared in our laboratory, at a concentration of 1 PPM. Fluorescence was followed as a function of time from dilution in two fluorometers. One was set up to excite fluorescence at 254 nm and to measure emission at 350 nm. The second was set up to excite fluorescence at 350 nm and to measure emission in a broad band from 410 to 550 nm. The crude oils showed an increase in fluorescence of 30% in 10 minutes, which leveled off at an increase in fluorescence of 50% in 40 minutes when excited at 254 nm. Fluorescence did not change with time when the sample was excited at 350 nm. The #2 fuel oil showed a similar, but smaller effect. It is possible that this effect is due to a slow partitioning of soluble fluorescent materials from the emulsion phase to the water soluble phase. (See 6. Solvent Effects, under MEASUREMENTS, below.)

SAMPLING

Sampling is discussed under the following headings:

1. Oil in the Water Column, with a Continuous-Flow Fluorometer.

2. Oil in the Water Column with “Grab” Samples.

Attempts to quantify particulate petroleum residue in water using nets have been reported (56, 57). Results were extremely variable and will not be further discussed.

Sampling problems associated with oil in sediment, organisms, air and on the land are discussed in the references cited in the sections entitled OIL IN SEDIMENTS, OIL IN ORGANISMS, OIL IN THE AIR and OIL ON THE LAND, above.

1. Oil in the Water Column, with a Continuous-Flow Fluorometer.

A continuous-flow, deck-mounted fluorometer may be used with either a fixed probe or with a towed probe and depressor. (See 1. Pumps, in EQUIPMENT, AUXILIARY, below.)

For relatively shallow work, the delay caused by the tubing from the probe to the instrument is negligible. For example, if a 1/2" ID garden hose is used with a six-gallon-per-minute pump, the time delay is only 0.1 second per foot of hose length. This is what was used in the South San Francisco Bay tests described in THE GOOD NEWS!, above. The time delay was under one second.

Contrary to expectations, we have not encountered any problems with oil holdup in hose or pump. Tests on oil holdup were run prior

to an experimental oil spill near Victoria, with similar results (58).

Thus, for shallow work, the continuous-flow fluorometer shares the advantage of rapid response with the towed submersible fluorometer.

It also shares the advantage that contamination problems associated with individual “grab” samples are avoided.

As a bonus, “grab” samples may be collected at the exhaust line of the fluorometer for other studies.

2. Oil in the Water Column with “Grab” Samples.

There are only two cases where this technique has an advantage - for occasional very deep samples and where sensitivity must be enhanced by extractive techniques.

Extractive techniques are discussed under EXTRACTION, above.

Sampling problems, sample preservation and special sample bottle designs are discussed (6, 10, 27, 59, 60, 61, 62).

MEASUREMENT

It is very important that the standard and the unknown be handled in the same way and be measured under the same conditions. Conditions to be considered include:

1. Temperature.

The temperature coefficient of fluorescence depends on the specific molecule involved, but - 3% per degree centigrade is not uncommon.

In addition, when oil is present as an emulsion, temperature can affect the amount of material transferred from the emulsion to the liquid phase. This can affect fluorescence. (See Solvent Effects, below.)

Where possible, maintain the standard and the unknown at the same temperature.

2. Dissolved Oxygen.

The presence of dissolved oxygen can reduce fluorescence.

Studies of benzene, naphthalene, anthracene, pyrene, fluoranthene and benzo(e)pyrene in water showed a significant drop in fluorescence as a function of dissolved oxygen (8, 63). This effect is much larger in organic solvents, which can hold more dissolved oxygen.

3. Concentration Quenching.

When the amount of oil present in water or other solvents is below about 1 PPM, fluorescence is proportional to the amount of oil present.

Above this level, fluorescence may or may not be proportional to the amount of oil present. The major cause of this nonlinearity is the absorption of the light used to excite fluorescence by the sample - before it enters the part of the sample in which the fluorescence is measured.

The point at which nonlinearity becomes significant depends on instrument design considerations. These include optical path length and the detailed design of the optical chamber.

The point at which nonlinearity becomes significant also depends on the way the instrument is set up. This includes the choice of excitation and emission wavelengths and is determined by the choice of lamp, excitation filter and emission filter.

The point at which nonlinearity becomes significant also depends on the nature of the sample. Where an oil emulsion is present, the size of the oil particles is important. In all cases, the optical extinction coefficient of the sample of the chosen excitation and emission wavelengths is of major importance. If the extinction coefficient is high, concentration quenching will start at low concentrations.

Frank (64) found significant nonlinearity when exciting at 290 nm for #2 fuel oil at 30 PPM, for #6 fuel oil at 6 PPM, for Bachaquero crude at 6 PPM and for Iran-Gach crude at 16 PPM. When exciting at 340 nm, the limit for #6 fuel oil was 7 PPM; Bachaquero crude, 18 PPM and Iran-Gach crude, 25 PPM. These measurements were made with the oil completely dissolved in cyclohexane.

In tests with #2 fuel oil emulsified in water and excited at 254 nm, we found significant nonlinearity at 2 PPM, but a calibration curve could be used to 10 PPM. In similar tests on Prudhoe Bay crude excited at 350 nm, nonlinearity started at 50 PPM and a calibration curve could be used to about 200 PPM.

4. Absorption Quenching.

The presence of a fixed amount of materials that are not associated with the oil but that do absorb light at the excitation or emission wavelengths or at both wavelengths will cause a reduction in sensitivity but will not introduce nonlinearity.

This effect is usually very low. In tests in South San Francisco Bay, we estimated the reduction in sensitivity in heavily phytoplankton-laden water to be only 10% when exciting at 254 nm. This estimate was based on separate spectrophotometric measurements of absorbance.

If a sample that is representative of the water in which oil is to be located but that contains no oil is available, it should be used for preparation of the standard. Absorption quenching effects will then cancel out.

5. Suspended Solids.

Suspended solids that do not truly absorb light at the excitation and emission wavelengths will have very little effect on fluorescence.

Carbon “fines” and other similar highly absorbing materials will affect fluorescence measurements, as discussed under Absorption Quenching, above.

The effect of these materials may be canceled out, if a sample representative of the water in which oil is to be located but that contains no oil is available. It should be used for preparation of the standard.

6. Solvent Effects.

The degree of fluorescence of a material depends on the molecular structure of the fluorescent material, the molecular structure of the solvent and the presence of other dissolved materials.

For example, carbon tetrachloride is reported to quench the fluorescence of oils (6). If used as an extractant, it must be completely removed by evaporation before the oil is redissolved for measurement.

In some cases, this quenching effect can be used to advantage. Proper choice of solvent can reduce and in some cases nearly eliminate the fluorescence of interfering materials (65).

Fluorescent materials exhibit different degrees of fluorescence when dissolved in hydrocarbons and when in true solution in water. This can cause some interesting problems when an emulsion is formed and diluted. As the water-soluble fractions move from the oil phase to the water phase of the emulsion, the degree of fluorescence should be expected to change. Oxygen-quenching effects should change at the same time.

7. Solvent Impurities.

It should be remembered that the amount of oil present in a solvent used for extraction or present after redissolving a residue will often be in the low parts-per-billion range. The presence of fluorescent impurities in the extractant or the solvent can interfere with the measurement of oil. The amount of impurities often varies widely from supplier to supplier (66).

8. pH.

Fluorescence is often sharply altered by pH. The unknown and the standard should always be at the same pH.

9. Sunlight.

Sunlight and room light (especially fluorescent light) cause deterioration of unknowns and standards. The effect of light depends on the solvent used (6, 27, 33, 67).

10. Salt.

Salt concentration equal to that found in sea water was shown not to affect the fluorescence of naphthalene, anthracene, pyrene and fluoranthene (63).

DATA COLLECTION AND INTERPRETATION

This section discusses a few very practical points that have come to our attention while making continuous-flow measurements of oil in the ocean.

1. BLANK Suppression.

We strongly recommend against using the automatic BLANK subtract feature available on all Model 10 Fluorometers in oil studies. Just turn the BLANK knob full counterclockwise and forget it.

Normally, fluorescence consists of two components. One is the underlying fluorescence of water (the Raman fluorescence), plus a relatively constant underlying fluorescence due to interfering fluorescent materials. In dye dispersion studies, for example, this underlying background fluorescence may be easily determined and corrected for by proper adjustment of the BLANK control. Readings will now be directly proportional to dye concentration.

In studies of oil in water, there is no sure way of getting a true background reading. If background fluorescence is overestimated when setting the BLANK knob, data will be lost.

As an example of how this can happen, we checked the fluorescence of Mountain View, California, tap water and of a new bottle of deionized water, using #2 fuel oil as a standard. The Mountain View tap water was lowest at 27 PPB, oil equivalent. The deionized water was expected to be lower in fluorescence than the tap water. It showed an oil equivalent of 34 PPB.

If we had assumed that the deionized water was free of background fluorescence, set the BLANK knob accordingly and made a survey in clean ocean water, all data in the clean water would have fallen below zero and been lost.

2. Recorders.

Oil in water is patchy and unpredictable. Experiments should be designed so that they may be rapidly revised in response to data generated.

A recorder that allows you to visualize what happened over the last 15 minutes is extremely useful. A chart speed of about 0.1 inch per minute per knot of cruising speed is about right. You should be able to write time and position and other data directly on the chart.

3. Communication.

Good communication between the person at the recorder and the person navigating the vessel is vital to experiment modification.

4. Position.

The ideal combination for data reduction at a later time is a data logger that accepts electronic position information, fluorometer output, time and other survey data.

In many situations you can get excellent data by cruising on straight lines from one known position fix to another. Note the time at each position fix on the recorder chart paper. Consider cruise speed to be constant to correlate intermediate positions with recorder data. You will then be able to plot oil as a function of position, on a navigational chart.

EQUIPMENT RECOMMENDATIONS, TURNER DESIGNS

1. Long-Wavelength Excitation.

Where high concentrations of crude oils or very heavy oils are to be studied, long-wavelength excitation may be used. (For greater sensitivity, see Short-Wavelength Excitation, below).

In our tests with emulsions of Prudhoe crude oil in water, we found the limit of detectability to be about 0.1 PPM, the linear range to extend to about 50 PPM and the useful range using a calibration curve to extend to about 200 PPM.

We have not made tests with extracted heavy oils, but would expect the limit of detectability to be about 10 PPB, and the linear range to extend to about 5 PPM, in the final solution. Since the final solution may be diluted, there is no upper limit to the useful range.

If you can use long-wavelength excitation, very considerable cost savings will result, since a borosilicate sample system, rather than an expensive quartz sample system, required at shorter wavelengths, may be used.

Order the 10-302 Oil Accessory Kit, Long Wavelength. It includes a lamp and spare lamp and all filters to provide excitation at 350 nm and to allow measurement of fluorescent emission in a wide band extending from 410 to 550 nm.

Refer to Borosilicate Sample Systems, below.

2. Short-Wavelength Excitation.

For all situations where #2 fuel oil or lighter oils are to be sensed, excitation at 254 nm and emission at 350 nm is mandatory. This is because the light oils contain very little of the three- and four-ring aromatics that are sensed by the long-wavelength excitation (30).
For all situations where an emulsion is not present, excitation at 254 nm and emission at 350 nm is mandatory. The heavier aromatics

detected by long-wavelength excitation are very slightly soluble in water (below 0.5 PPM). Thus, unless an emulsion is present, these materials will be present at a maximum concentration which is very near the limit of detectability using long-wavelength excitation.

In contrast, the naphthalenic fractions are soluble to about 20 PPM (8, 28). These are the materials sensed by short-wavelength excitation. They may be present in the water column in the absence of an emulsion at up to 4000 times their limit of detectability of about 5 PPB.

In our tests using short wavelength excitation and #2 Fuel Oil emulsions in water, we found the limit of detectability to be about 2 PPB, the linear range to extend to about 2 PPM and the useful range, using a calibration curve, to extend to about 10 PPM.

Order the 10-301 Oil Accessory Kit, Short Wavelength. It includes a lamp and spare lamp and all filters to provide excitation at 254 nm and to allow measurement of fluorescent emission at 350 nm.

Refer to Quartz Sample Systems, below.

3. Borosilicate Sample Systems.

Borosilicate sample systems are useful only when detecting high concentrations of crude oil or very heavy oils, with long-wavelength excitation. See Long-Wavelength Excitation, above.

The Rack-Mount Fluorometers (models 10-000 and 10-000R) and the Field Fluorometers (models 10-005 and 10-005R) are normally equipped with a borosilicate continuous-flow cuvette system.

For “grab” samples and for each calibration of the Rack-Mount Fluorometers and the Field Fluorometers, the 10-027 Cuvette Adaptor Kit may be used. The sensitivity of the 10-027 Cuvette Adaptor Kit is identical to the sensitivity of the continuous-flow system, normally supplied with the Rack-Mount and Field Fluorometers. This simplifies calibration procedures and data reduction, when both continuous-flow and grab samples are used in a single experiment.

Where extractive techniques are used, the 10-030 Cuvette Holder should be used. The minimum sample volume is only 4 ml.

4. Quartz Sample Systems.

For continuous-flow work with short-wavelength excitation, a quartz sample system is required.

For Rack-Mount or Field Fluorometers, specify that they shall be supplied without the 10-020 High-Volume Continuous-Flow System, and with either the 10-007 High-Volume, Quartz, Continuous-Flow System or the 10-330 High-Volume, Quartz, Continuous-Flow System with Clean Out.

Existing owners of either the Rack-Mount or Field Fluorometers, if they have the standard (borosilicate) 10-020 High-Volume Continuous-Flow System, may purchase the 10-009 Quartz Replacement Kit. This is a direct replacement for the borosilicate cell in the 10-020 or its related 10-016 (with Clean Out).

Where extractive techniques are used, the 10-030B Cuvette Holder may be used. 10-297 13 x 100 nm Quartz Cuvettes must be ordered separately. The minimum sample volume is only 4 ml.

If you have a 10-030 or 10-030A Cuvette Holder at present, the windows and mirrors may be pried off. The result will not be pretty, but it will work.

The best system for measurement of extracted samples is the 10-027A Cuvette Adaptor Kit and 10-295, 25x100mm Quartz Cuvette. This requires a minimum volume of 25 ml.

EQUIPMENT, AUXILIARY

The following comments are not intended to be exhaustive or to endorse any product. But - we do want to pass our experience on to you.

1. Pumps.

Flow rate (velocity of sample through the instrument) has absolutely no effect on the reading of the instrument.

An occasional air bubble will cause the reading to jump but will not cause any serious loss in data. A steady stream of bubbles will cause serious errors.

Dissolved oxygen can be released if water is highly saturated and water pressure is reduced by pumping.

With these factors in mind, it can be seen that a submerged centrifugal pump at the inlet to the sample system has a lot of advantages. Air bubbles cannot leak into pump seals, since the pump is submerged. Positive pressure is maintained on the entire system, keeping dissolved air in solution, and minimizing leaks.

Another virtue of centrifugal pumps is that they can be throttled back without damage. Actually, restricting flow on a centrifugal pump reduces its power input.

One such pump available from Turner Designs is the 10-590 Bilge Sample Pump, Submersible Centrifulgal type, 450 gallons per hour maximum, 300 gallons per hour at 3 ft. head, 12V DC operation at 2 amps. Maximum head is 5 ft.

A point that should be watched is that there will be suction on the bearings, and of course, since we are measuring oil, no oil from pump bearings can be tolerated.

Where plenty of AC power is available, a peristaltic deck-mounted pump has advantages. It is self-priming and has no seals to introduce air or oil. Capacity must of course be matched to the sample system, since it is a positive-displacement pump and may not be throttled back.

To minimize release of dissolved air, the pump should be mounted as low as possible in the boat and as close to the inlet line as possible.

One such pump we have seen in service is the Model LG-301 pump made by the Little Giant Pump Company, 3810 N. Tulsa St., Oklahoma City, OK 73112. By proper choice of model and tubing size, flow rates of about 0.5, 1, 3 and 5 gallons per minute may be obtained with this series of pumps.

2. Pumping Rate.

The pumping rate is set by the speed of response you need. The lower the rate, the lower the chance of release of dissolved oxygen and the less the chance of leaks. The price paid is in increased delay between the sample inlet and the fluorometer.

A handy number to remember is that a 1/2" ID garden hose holds about 0.01 gallon per foot. If, for example, you had 20 feet of such hose and were pumping at 3 gallons per minute, the delay time would be 0.01 x 20 - 3 or 0.067 minutes or 4 seconds.

3. Intake Screen.

A perforated pipe wrapped with screen mesh does a fine job.

4. Sample Hose.

We found no problems with absorption and release of oil from the walls of common plastic garden hose. The type we used had a braided green exterior and a smooth black liner.

Another type of hose that looks very good is the type V-HT tubing made by Thermoplastic Scientific, Inc., 57 Stirling Rd., Warren, NJ 07060. It consists of a cross-linked polyethylene liner, coextruded with an EVA outer shell, to give both good chemical and physical properties. It was shown to have low absorption of m-Cresol (71), but we do not know of similar tests with petroleum.

Soft vinyl tubing, such as Tygon(R), should be viewed with suspicion. Soft vinyls often contain fluorescent plasticizer and have been shown to absorb and desorb other fluorescent materials quite rapidly.

5. Recorder.

This is one place where you should really go first class!

A wide chart with lots of room to write is important. A flat bed that gives good support for writing is important. A reasonable range of chart speeds is desirable. (We find that about 0.1"/min. of chart travel per knot of cruising speed is a good choice.) One channel for reading and one channel for range is a luxury. Normally, for oil work, range changes will be rare and can be noted on the chart.

We suggest the Turner Designs 10-LM Series Recorders with 10-LM197 Paper Take Up.

ORDERING INFORMATION

Special items for oil in the environment only are listed below. See the brochure entitled Field Fluorometry for items not covered below.

10-295 - 25 x 100 nm Quartz Cuvette.

For use with 10-027 Adaptor. A low-fluorescence quartz cuvette required at excitation wavelengths below approximately 320 nm.

10-030B - Cuvette Holder, 13 x 100 mm.

Discrete sample. No windows. Required at wavelengths below 320 nm.

Cuvettes must be ordered separately. For quartz cuvettes, order 10-297 13 x 100 mm Quartz Cuvettes. May be used at wavelengths above 320 nm, with 10-031 - 13 x 100 mm Selected Cuvettes.

10-297 - 13 x 100 mm Quartz Cuvette.

For use only with the 10-030B Cuvette Holder. These are low-fluorescence quartz cuvettes, and are required at excitation wavelengths below 320 nm.

10-300 - Filter, Soft Glass.

10-301 - Oil Accessory Kit, Short Wavelength.

Consists of one 10-046 Clear Quartz Lamp, F4T5 and one spare lamp; one 10-038 color specification 254 interference filter; one 10-064 color specification 7-60 filter and two 10-300 soft glass filters.

May only be used with a quartz cuvette.

10-302 - Oil Accessory Kit, Long Wavelength.

Consists of one 10-049 Lamp, Near UV, F4T5 and one spare lamp; one 10-059 color specification 2A filter; one 10-068 color specification 4-96 filter; one 10-069 color specification 7-37 filter and one 10-300 soft glass filter.

Recommended only for high concentrations of emulsified crude oil.

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