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Comparison of UV Fluorescence and Gas Chromatographic Analyses of Hydrocarbons in Sediments from the Vicinity of the Argo Merchant Wreck Site

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On December 15, 1976, the tanker ARGO MERCHANT ran aground on Fishing Rip of Nantucket Shoals off the Massachusetts coast. Within one week she had broken into three parts. The stern and midsection remained aground near the original point of impact and the bow section floated off, eventually sinking 2.8 km SE of the other two sections. During that week, about 28 x 10^3 metric tons of No. 6 fuel oil were spilled into the ocean. In order to determine the extent of possible sediment contamination in the vicinity of the wreck site and on Little George's Bank, the University of Rhode Island (URI) organized five cruises to the area. Chemists from the U.S. Coast Guard Research and Development Center (USCGRDC) using u.v. fluorescence spectroscopy conducted on-board hydrocarbon screening of water and sediment samples collected on three of these cruises. The data obtained from the first two survey cruises, examining a 4000 km^2 area, indicated that the sediment samples were contaminated with ARGO MERCHANT oil only around the wreck sites (Coast Guard chemistry report, GROSE & MATTSON 1977). On the basis of these findings, a detailed sediment survey of the wreck site area was planned and conducted on URI's oceanographic vessel R/V ENDEAVOR. As in the previous cruises, USCDRDC chemists screened the sediments for their hydrocarbon content immediately after collection. These data were used to assign additional stations to provide more detail within the planned sampling grid. In addition to the analyses provided by the Coast Guard, the sediments were also analyzed at the Graduate School of Oceanography (URI) using gas chromatography. Since both groups analyzed samples from the same container, it was hoped that the two sets of data would provide an opportunity to compare, using actual field samples, two different analytical techniques for determining sediment petroleum hydrocarbon concentrations. The environmental significance of these studies has been discussed elsewhere (HOFFMAN & QUINN 1978, 1979, JADAMEC 1978).

METHODS

Sampling. Surface sediment samples were collected from the Nantucket Shoals-ARGO MERCHANT wreck site area aboard R/V ENDEAVOR (EN-005, February 22-27, 1977) with a Smith-McIntyre grab sampler. The locations of the sampling sites are given in Figure 1. One half of each grab sample was preserved in formalin for biological studies (PRATT 1978) and the other half was used for chemical analyses. Successive subsamples of the chemical analysis portion of the sampler were placed into individual solvent rinsed Mason jars. The depths noted in the results section are estimates of the different depths in the grab sampler from which these individual subsections were taken.

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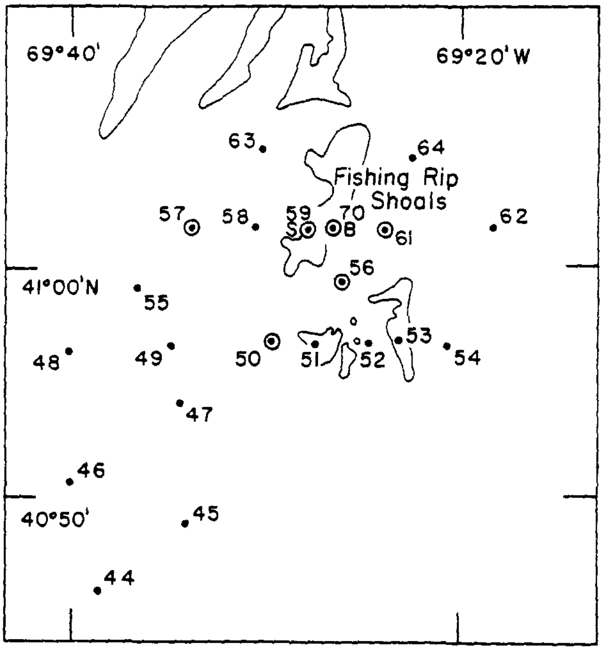

Figure 1. Station locations of EN-005 (February 22-27, 1977). The "S" (Station 59) is the location of the ARGO MERCHANT stern and mid-sections and the "B" (Station 70) is the location of the ARGO MERCHANT bow section. The circled stations are those which were analyzed by both UVF and GC methods.

No attempt was made to thoroughly homogenize the samples in the jars. A small portion (10 cc of wet sediment) was removed from the jar for on-board screening by u.v. fluorescence techniques, and the remainder of each subsample was frozen and stored for gas chromatographic analyses.

U. V. Fluorescence (UVF) Analysis. All sediment samples were analyzed by synchronous excitation/emission fluorescence spectroscopic techniques as previously described by GORDON & KEIZER (1974). Samples were prepared for analysis by extracting 10 cc of wet sediment with 10 mL of spectroquality hexane similar to the procedure described by MILES et al. (1977). All synchronous excitation/emission analyses were performed using a fully corrected Farrand Mark I spectrofluorometer using an excitation bandpass of 10 nm, and emission bandpass of 2.5 nm, and a scan speed of 30 nm/min with a constant offset of 25 nm between the excitation and emission monochromators from 280 to 480 nm. Estimates of hydrocarbon concentration were made using the ARGO MERCHANT oil as the standard.

Gas Chromatographic (GC) Analysis. Only selected sediment samples were analyzed. A detailed description of the analytical techniques used are given in HOFFMAN & QUINN (1978). Briefly, the samples were thawed; 200 g aliquots were weighed; n-C_{20} and n-C_{22} internal standards were added; the sediments were then refluxed with a mixture of 0.5 N

KOH-MeOH and toluene (70:30). After filtration, the extract was partitioned into petroleum ether. The petroleum ether-toleune phase was evaporated to dryness, charged to a silica gel-alumina-Cu column and eluted with a 95% petroleum ether-5% toluene mixture. A small amount of the resulting eluent was analyzed on a gas chromatograph (FID), equipped with dual packed columns (2m, 2.2 mm i.d. stainless steel containing 10% SP-1000 on Supelcoport, 80/100 mesh). The hydrocarbons which eluted from the column between n-C_{14} and n-C_{34} were quantified by comparing the areas of the sample components with the areas of the internal standards.

RESULTS

The analytical results of the two sets of data are given in Table 1. Linear regression analysis, with no zero or trace values considered, indicated a regression equation as follows:

$$\text{GC values} = 0.510 \times \text{UVF values} - 0.76 \quad (n = 13,\ r = 0.66). \tag{1}$$

When zero values and trace values were considered, the regression equation was:

$$\text{GC values} = 0.498 \times \text{UVF values} + 0.26 \quad (n = 24,\ r = 0.72) \tag{2}$$

However, it should be pointed out that the reason for the somewhat significant correlation coefficients (r) is the higher values. When values over 100 µg/g were eliminated, no significant correlation was found and the regression equation was:

$$\text{GC values} = 0.078 \times \text{UVF values} + 5.84 \quad (n = 10,\ r = 0.28) \tag{3}$$

In addition, if the alternative values for samples including tar particle contributions (note 5 on Table 1) are used, the regression equation was:

$$\text{GC values} = 0.284 \times \text{UVF values} + 25.5 \quad (n = 24,\ r = 0.16) \tag{4}$$

DISCUSSION

The URI laboratory has participated in several successful intercalibrations between investigators all using GC analysis techniques (FARRINGTON et al. 1976, LAKE et al. 1979, WADE & QUINN 1979). Such success in hydrocarbon analyses by GC is not universal however, especially when low concentrations are present (HILPERT et al. 1978). Intercalibrations using different analytical techniques for hydrocarbons are scarce and generally unsuccessful. ZSOLNAY (1978) reported results to an intercomparison of GC and high performance liquid chromatography utilizing a u.v. absorption detector. There was no significant correlation between the results of the two techniques when analyzing organism tissues. He concluded that u.v. absorption measurements alone

TABLE 1

Sediment hydrocarbons in the vicinity of ARGO MERCHANT wreck site analyzed by two methods.

Station	Coast Guard UVF value[1] (ppm)	URI GC value[2] (ppm)
50(1) 0-1	0	<0.1
50(2) 0-1	0	0.8
56(1) 0-1	Trace[3]	1.2
56(2) 0-1	0	<0.3
57(1) 0-1	Trace	<0.1
59(1) 0-1	Trace	2.4[4](76)[5]
59(1) 1-3	3.5	0.5
59(1) 3-5	0	<0.1[4](49)[5]
59(3) 0-1	10	2.6[4](330)[5]
59(3) 1-3	0	<0.1
59(3) 3-5	6	<0.1
59(4)	0	0.3
61(2) 0-1	0.9	1.1
61(3) 0-1	0	0.7
70(1) 0-1	70	13.
70(1) 1-3	15	30.
70(1) 3-5	90	12.
70(1) 5-10	120	20.
70(2) 0-1	8.2	10.
70(2) 1-3	0	4.0
70(2) 3-5	10	5.6[4](35)[5]
70(4) 0-1	100	75.
70(4) 1-3	50	5.1
70(4) 3-5	120	120

[1] units are μg oil/g wet weight;

[2] units are μg HC/g dry weight. The average dry/wet weight ratio is 0.85;

[3] trace is defined as <0.2 ppm but above background;

[4] tar particles removed prior to analysis;

[5] tar particles included in the analysis.

cannot be used to monitor the non-point source petroleum concentrations in organisms. ZSOLNAY (1978) pointed out that interference from biogenic organic materials which also absorb in the u.v. range may affect the results, and that when hydrocarbons have been accumulated from several sources, the choosing of a standard is difficult. In a situation where the types of aromatics in the samples vary considerably, standardization is impossible. KEIZER et al. (1977) measured hydrocarbons in water samples using GC and u.v. fluorescence. Because they reported their GC values in units of ng/L of n-alkanes (not total hydrocarbons) and their UVF data in μg/L of estimated oil, they did not expect their values to agree. They found a correlation between the two sets of data in one of the four localities examined (Bedford Basin). They postulated that at this location the aliphatic hydrocarbons and the aromatic hydrocarbons were from the same source resulting in a correlation coefficient of 0.511 (n = 21) and suggesting the presence of petroleum derived hydrocarbons. At the other locations where no correlation between the two techniques was found, a biogenic source for the hydrocarbons was postulated.

As previously mentioned, in this study there was no significant correlation between the GC and UVF methods. Part of this lack of correlation was undoubtedly due to the inhomogeneity of the samples. As pointed out by HOFFMAN & QUINN (1978) and PRATT (1978) the hydrocarbons present in these samples was in the form of minute tar particles or oil droplets (0.1-2.0 mm in diamter) mixed inhomogeneously into the samples. The larger of these tar particles (1.0-2.0 mm in diameter) were shown to account for 83 to >99% of the total hydrocarbons in four of these samples (HOFFMAN & QUINN 1979). These particles account for the apparent poor reproducibility even when samples were taken from the same jar and analyzed by only one method. One sediment sample [70(4)0-1] was analyzed by the GC method three times, yielding values of 120, 70 and 36 μg total HC/g dry wt. (75 ± 41), a relative standard deviation of 55%. The usual precision of this procedure using more homogeneous sediment is ∿12% (HOFFMAN, unpublished data; BOEHM & QUINN 1978). Thus, the large variability exhibited in the replicates using one of the methods in this study is due to inhomogeneity of the samples. The sample inhomogeneity as reflected in the replicate GC determinations was present even though fairly large sample sizes were used (∿200 g). The presence or absence of just one tar particle in a given sample aliquot could affect the analytical results of 2 orders of magnitude (HOFFMAN & QUINN 1978). Clearly, the effect would be accentuated when smaller sample sizes were used. In the present intercomparison study, the agreement of non-zero values were always within one order of magnitude which, considering the nature of the samples, might have been fortuitous indeed. On cursory examination of the data in Table 1, it can be seen that the UVF data are generally higher than the GC data. The reason is that several of the samples were analyzed after their tar particles were removed. If the GC values for samples 59(1)0-1, 59(1)3-5, 59(3)0-1, and 70(2)3-5 were corrected for the additional hydrocarbons due to these tar particles the values change from 2.4, <0.1, 2.6 and 5.6 ppm to 76, 49, 330 and 35 ppm, respectively (Table 1). As noted by the regression equation 4, the correlation coefficient degenerates even further and one set no longer appears routinely higher than the other.

It is our opinion that the inhomogeneity in the samples used in this intercomparison study overwhelmed any effect due to analytical incomparability. Previously, sediment samples used for intercalibrations have generally been homogenized in a blender (WADE & QUINN 1979) or a cement mixer (HILPERT et al. 1978) and "muds" rather than "sands" are used. Effective homogenization of these coarse sands on shipboard would have been very impractical and would have greatly diminished the virtue of the speed of the onboard screening process. Such speed is necessary so that the data can be used to assign additional station locations while still at sea. Thus, some degree of inhomogeneity will persist in this type of study and coarse sands would obviously present the most difficult problem in this respect.

In addition to the lack of homogeneity, other factors which could lead to a lack of correlation should be mentioned.

(1) Sample size The UVF method used 10 cc of wet sediment (∿20 g dry weight) and the GC method used ∿200 g dry weight. If the sediment samples were completely homogeneous, the difference in sample size should have no measurable effect on the analytical results. However, the sediments were not homogeneous with regard to the distribution of tar particles. Therefore, a small amount of sediment containing one tar particle would yield different values than a larger amount of sediment with this same tar particle.

(2) Extraction techniques The UVF method used hexane at room temperatures to extract the hydrocarbons whereas the GC method used a methanolic-KOH and toluene mixture under reflux conditions to extract the hydrocarbons. While there is evidence that the extraction of wet sediment with hexane under reflux only returns about 10% of the weathered hydrocarbons extracted by methanol or methanolic KOH (HOFFMAN, unpublished data), fresh hydrocarbons may be extracted much more efficiently by hexane (J. GEARING, personal communication 1978). This question is currently under investigation. Hexane may be able to extract freshly added hydrocarbons while not efficiently extracting weathered or indigenous hydrocarbons. This discrimination could be of practical importance when the analyst is interested in only recently added hydrocarbons. Since, in the case of this study, the background levels of hydrocarbons were <0.1 - 0.3 μg/g, and the freshly added hydrocarbons were essentially unweathered ARGO MERCHANT oil (HOFFMAN & QUINN 1978) the use of different extraction techniques is probably not critical. Clearly, however, the use of different extraction techniques for recently added hydrocarbons warrants further study.

(3) Analytical techniques The instrumentation used for hydrocarbon quantification in this intercomparison study responds to different parameters. The UVF technique used by the Coast Guard responds to compounds which fluoresce, such as 2-5 membered ring aromatic hydrocarbons. Potential problems with this detection method include preferential weathering of aromatic hydrocarbons and interference by naturally occurring organic compounds which also fluoresce. There is evidence that only the lighter components of the oil were found in the water column shortly after the spill (JADAMEC 1978). While this indicates that some degree of preferential dissolution or fractionation of the fuel oil was taking place, perhaps at the surface,

the fingerprint obtained between the cargo oil and the sediment hydrocarbons by UVF was still very good. The potential weathering problem probably had little effect on the sediments examined in this study. Interference by naturally occurring fluorescing compounds was also at a minimum because the sediments of Nantucket Shoals were sandy with little organic matter associated with them.

GC analyses of hydrocarbons with appropriate isolation steps are not subject to interference by non-hydrocarbon organic material. Moreover, should preferential weathering effects occur, they are detected in the chromatograms and are thus taken into account when the values are calculated. But in intercomparison studies with other techniques, additional problems arise. In the GC method, only the hydrocarbons eluting from the column between n-C_{14} and n-C_{34} were quantified. Thus, the values are a lower limit for the total hydrocarbons. Since the ARGO MERCHANT cargo was a mixture of about 80% No. 6 and 20% No. 2 fuel oil, there was little contribution added by hydrocarbons eluting before n-C_{14} but there was evidence that hydrocarbons eluted from the column past n-C_{34}. Because isolation steps were used prior to GC, the non-hydrocarbon components of the oil were not measured. No attempt was made in this study to convert the hydrocarbon values obtained by GC to concentrations of ARGO MERCHANT oil in the sediment as reported in the UVF method. These two parameters, definition of elution range and the measurement of only hydrocarbons, are defined in advance of intercalibration exercises employing only gas chromatography. However, they become potential sources of error when other techniques are compared to the GC method.

The opinions or assertions contained herein are the private ones of the authors and are not to be construed as official or reflecting the views of the Commandant or the Coast Guard at large.

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REFERENCES

BOEHM, P. D. and J. G. QUINN: Est. Coast. Mar. Sci. 6, 471 (1978).

FARRINGTON, J. W., J. M. TEAL, C. C. MEDEIROS, K. A. BURNS, E. A. ROBINSON, J. G. QUINN and T. L. WADE: Anal. Chem. 48, 1711 (1976).

GORDON, D. C., JR. and P. D. KEIZER: Fisheries and Marine Service Technical Report No. 481, 1 (1974).

GROSE, P. L. and J. S. MATTSON (eds.) The ARGO MERCHANT Oil Spill: A Preliminary Scientific Report. NOAA Special Report, NOAA-ERL, Boulder, CO, (1977).

HILPERT, L. R., W. E. MAY, S. A. WISE, S. N. CHESLER, and H. S. HERTZ: Anal. Chem. 50, 458 (1978).

HOFFMAN, E. J. and J. G. QUINN: Proceedings of the Symposium in the Wake of the ARGO MERCHANT, Center for Ocean Management Studies, University of Rhode Island, Kingston, RI, 80 (1978).

HOFFMAN, E. J. and J. G. QUINN: Mar. Poll. Bull. 10, 20 (1979).

JADAMEC, J. R.: Proceedings of the Symposium in the Wake of the ARGO MERCHANT, Center for Ocean Management Studies, University of Rhode Island, Kingston, RI, 53 (1978).

KEIZER, P. D., D. C. GORDON, JR. and J. DALE: J. Fish. Res. Board Can. 34, 347 (1977).

LAKE, J. L., C. Q. DIMOCK and C. NORWOOD: Proceedings of the ACS National Meeting, Miami, FL. In press (1979).

MILES, D. H., M. J. COIGN, and L. R. BROWN: Proceedings 1977 Oil Spill Conference (Prevention, Behavior, Control and Clean-up), New Orleans, LA, (1977), p. 179.

PRATT, S. D.: Proceedings of the Symposium in the Wake of the ARGO MERCHANT, Center for Ocean Management Studies, University of Rhode Island, Kingston, RI, 131 (1978).

WADE, T. L. and J. G. QUINN: Mar. Environ. Res. In press (1979).

ZSOLNAY, A.: Wat. Air Soil Poll. 9, 45 (1978).