

Oil Spill Identification and Remote Sensing¹

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This chapter is comprised of two distinct parts. The first is a review of the state of the art in oil spill identification techniques. It includes significant developments that have firmly established oil fingerprinting as a valid approach to identification of oil spill sources. These include: increased understanding of weathering phenomena, refinement of analytical techniques and pattern recognition techniques for oil comparison, adoption by ASTM of new standard methods for spill identification, establishment of a Central Oil Identification Laboratory (COIL) and satellite Field Oil Identification Laboratories (FOIL) by the U.S. Coast Guard, and four successful tests of the analytical methodology in court. The second part of this chapter is a brief account of development of planned and operational remote sensing systems as applied to oil spill detection, identification, and mapping.

Since the author's review on "Oil Spill Identification" (1, 2), a number of significant occurrences have firmly established oil fingerprinting as a valid approach to the identification of spill sources. These include increased understanding of the effects of weathering on oils, continued refinement of various analytical techniques, continued refinement of computer pattern recognition techniques for comparison of oils, the adoption by ASTM of new methods of analysis of waterborne oils (3, 4, 5), the establishment of a Central Oil Identification Laboratory (COIL)

¹The opinions or assertions contained herein are the private ones of the writer and are not to be construed as official or reflecting the views of the Commandant or the Coast Guard at large.

by the U.S. Coast Guard with satellite Field Oil Identification Laboratories (FOIL) throughout the country, and, most significantly, four successful tests of the analytical methodology as evidence in courts; three in federal courts and one in a New York State court. This, coupled with airborne surveillance by the Coast Guard, has provided sufficient deterrence, for example, to stop significant spills in the Florida Straits since July 1977 (6). Kleineberg (7) recently reviewed the operational oil identification techniques employed by the U.S. Coast Guard to identify the sources of spilled oil.

Interest in the impact of spills has been given additional impetus by the *Argo Merchant* disaster in December 1976 and by the more recent (March 1977) grounding of the *Amoco Cadiz* off the coast of France, which resulted in the largest oil spill ever recorded (over 200,000 tons of light crude oil).

The problem of oil spills is here to stay. Spill incidents in and around U.S. waters have been averaging between 10 and 11 thousand per year in recent years (8), with 80% of the spills being less than 800 gal (9). About 350,000 tons of oil are being spilled accidentally each year. For the year 1975, the Coast Guard estimated that four times that amount was dumped deliberately by oil tankers in the normal course of operations—cleaning cargo tanks or emptying ballast water (10). Sleeter (11) cites National Academy of Sciences figures for the same year as showing six times as much oil per year from cleaning operations as from spills (tanker and nontanker accidents). Oostdam and Anderlini (12) point out that although spectacular oil spill accidents are well documented, very little has been published concerning the level of pollution along the coasts of the world's major oil-producing countries in the Middle East, where the specter of a major oil spill in the semienclosed gulf between Iran and Arabia becomes a frightening possibility.

To assess the full short- and long-term ecological impacts of major oil spills, an immediate and coordinated scientific response is required. To delineate the requirements for such a response, the Montauk Workshop on Oil Spill Studies: Strategies and Techniques was convened in February 1976 (13) and dealt with such topics as information management, chemistry, and the effects on plankton, benthos, fish, birds, marine mammals, and sea turtles. The Conference on Assessment of the Ecological Impact of Oil Spills (held by the American Institute of Biological Sciences and cosponsored by the American Petroleum Institute and seven government agencies at Keystone, Colorado, June 1978) addressed the ecological studies of numerous recent major oil spills. The quality of information improved with each spill as experience was gained and the degree of coordination was increased. Immediate, well-integrated response in the case of the *Amoco Cadiz* resulted in better sampling and a

clearer picture of the oil distribution. The scope of this paper does not permit further discussion of fate and effects of oil spills other than to cite a key bibliography (14) soon to appear that has over 1200 references, each with abstracts.

New responses for cleanup are required; one of these is the use of chemical dispersants. Obviously, if dispersants come into common use, the question must be answered whether any given analytical technique can still identify the source of the spill. At least two studies are underway in this area: one by the Coast Guard and the other by the University of Rhode Island, under a Department of Energy contract.

Legal Aspects

Oil spills have a large economic impact on fisheries and resort and recreational areas, with the result that legal settlements are frequently large. Ultimately, the oil spill analyst must also be a forensic chemist: this author addressed the oil spill chemist's philosophy and technical approach in a presentation to the American Bar Association's Session on Marine and Tanker Problems (15).

Sleeter (11) examined the evidentiary aspects of the techniques used for oil fingerprinting and cited one case where the fingerprinting techniques resulted in a pretrial liability settlement. He concluded that a significant amount of experience has been gained in fingerprinting and that it meets the FRYE test of having "gained general acceptance in the particular field in which it belongs." He thus concludes that "the case for the admissibility of fingerprint identification seems strong," since the court in *Stifel* had noted "neither newness nor lack of absolute certainty in a test suffices to render it inadmissible in court . . . (and) . . . every useful new development must have its first day in court."

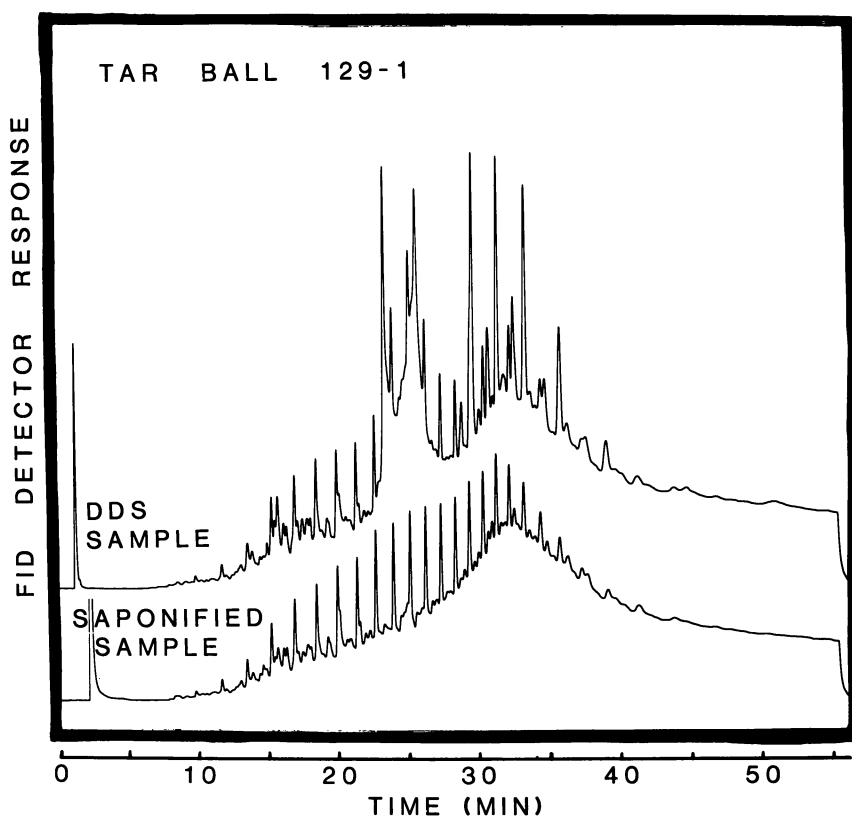
Since Sleeter's review, several cases have been tried using chemical fingerprinting to determine the source of an oil spill. The three cases tried in 1977 emphasized the importance of documentation, beginning with the taking of the sample (long before the chemist becomes involved) and requiring an unbroken chain of custody until the sample is disposed of.

At the time of a spill investigation, it is hard to realize that the case may not appear in court for three to five years, at which time the fallibility of the human memory becomes agonizingly apparent. The result is that everything must be fully documented. In the first federal court test of chemical oil fingerprinting conducted in 1977 in Houston, the judge made it clear that the on-scene investigation was not thorough and made equally clear that the scientific testimony was persuasive. Judge Finis E. Cowan stated, ". . . if anything, the physical facts lean in favor of the defendant.

This court is basing its ruling entirely and one hundred percent on the (scientific) testimony . . . which the court finds to be credible and believable and scientifically reliable.”

Several civil court cases have been decided on the basis of a single analytical method. This is certainly warranted when the results are unequivocal. The first citable case is that of *U.S. vs. Slade, Inc.* (16), in which the unreported case of Judge Cowan's is referenced. Both cases used gas chromatography with flame ionization and flame photometric (sulfur) detection as the only analytical method.

The merit of the multimethod approach lies in the added confidence given the results from a concurrence of several methods. The multimethod approach is most desirable when contaminants picked up by the spill may



U.S. Coast Guard

Figure 1. Gas chromatograms of a contaminated Cape Cod tar ball before (upper curve) and after (lower curve) cleanup by a saponification technique

obscure the results by one or more methods. The presence of contaminants that may come from biologically generated glycerides, bilge cleaners, etc., will be apparent from the nonpetroleum aspects of the fingerprint by any given method. Some specific methods used, however, may be insensitive to contaminants and thus allow for designation of a match despite the presence of contamination in one of the two samples compared.

Aside from having backup methods available in the event of interference, it is possible in many instances to clean up the sample to obtain the true petroleum fingerprint. One such method is that of Frame et al. (17), in which saponification is used for sample cleanup. An example of the use of saponification is shown in Figure 1, which shows gas chromatograms of a tar ball from Cape Cod before and after cleanup. These analyses were conducted on a 3-m packed column with 10% OV-101. The temperature was programmed from 75°–325°C at 8°C/min and held isothermally at the maximum temperature for 32 min. The helium flow rate was 30 mL/min. After the saponification treatment, it is clear that a normal petroleum-type chromatogram that can be compared with suspected sources is obtained. In this instance, the tar ball was shown not to originate from either the *Argo Merchant* or the *Grand Zenith*, as first thought, thus releasing the shipowners from liability.

A major legal aspect is the adoption of standard methods for oil fingerprinting such as the ASTM consensus standards, because it facilitates acceptability of the findings as evidence in court cases.

Recent Developments in Spill Fingerprinting Methodology

Overview. The Coast Guard recently published a definitive manual on spill identification (18) that included sections on oil sampling, sample handling and transmittal, simulated weathering of oils, identification by gas chromatography (GC), fluorescence spectroscopy (FL), low-temperature luminescence (LTL), infrared spectroscopy (IR), thin-layer chromatography (TLC), and high-pressure liquid chromatography (HPLC). The basic Coast Guard oil identification system is comprised of GC, FL, IR, and TLC methods. Sections also included are a field manual for infrared oil spill identification, a field classification of oils by infrared spectroscopy, and one on safety aspects of the laboratory procedures.

The ASTM has already published a “preamble” to oil identification (19) and methods on preservation of samples (20), elemental analysis (21), and infrared analysis (22), in addition to the GC and FL methods (4, 5) and sample preparation methods (3) previously mentioned. Widespread adoption of these carefully developed methods and their under-

lying philosophy in the analytical approach used should lead to more uniform practices.

The Coast Guard has selected two complementary methods for use by its Central Oil Identification Laboratory (COIL), which is an operational unit devoted full time to oil spill fingerprinting, namely LTL and HPLC. Other methods that have been used are atomic absorption spectroscopy (AA), emission spectroscopy (ES), X-ray fluorescence (XRF), gas chromatography-mass spectrometry (GC-MS), mass spectrometry (MS), and limited wet methods of analysis (23).

Following is a look at the most recent developments in oil spill identification by several of these oil fingerprinting techniques, including sampling and a discussion of an interlaboratory study on the effects of weathering on the capability to match oils.

Sampling. Representative samples of spills and suspect oils are a must to obtain definitive results in oil matching. Teflon strips and Lipopore screens (24) continue to show the most promise for sampling slicks for laboratory analysis. The Lipopore screen, manufactured by Hydroil Corporation, of Plymouth, New Hampshire, is undergoing extensive field testing by the operational Coast Guard. The Lipopore screen is used to admit oil, with the exclusion of water, into a cannister lowered to the water surface by means of a monofilament line. The cannister is replaced into its shipping jar for transmittal back to the laboratory.

Weathering. Most of the analytical methods selected for oil spill fingerprinting work very well on "neat" (unweathered) oils. When oil is spilled on water, it immediately starts to change composition as a function of the effects of water solubility, evaporation, temperature, sunlight, wind and wave action, bacterial action, etc. Therefore, most of the development of instrumental methodology requires taking weathering into account, on the premise that the weathering changes of a given oil are smaller in magnitude than differences between two different oils of the same type. To a large extent this is true, although it may not be in the very light petroleum products.

The Coast Guard, perceiving a need to test its fingerprinting methods and those of ASTM, conducted a large-scale interlaboratory (25) weathering study to see the effects of weathering on four different oil types (No. 2, No. 4, and No. 6 fuel oils, and a Louisiana crude) weathered over four days, sampling daily. Sixteen laboratories, most of them active on ASTM task groups, participated.

The interlaboratory study showed overall that the GC procedure gave the best results, followed closely by IR and then FL. When the IR spectra were interpreted by those expert in oil spill matching, the IR results were significantly better than GC or FL, indicating that IR is the method most influenced by "expert" interpretation.

The major conclusion of the interlaboratory study confirms our growing belief in the necessity for a simple, standard method for accelerated or simulated weathering in the laboratory of suspect samples prior to comparing them with spill samples. All of the methods were better able to match weathered samples with other weathered samples of the same oil than they were to the unweathered oil.

Numerous workers have studied simulated weathering. Brown et al. (26) and Frankenfeld (27) conducted two-year studies under Coast Guard contract on the weathering of oil and devised some effective rapid simulation methods that could be the basis for future standardized methods. Ahmadjian et al. (28) studied simulated weathering by infrared spectroscopy. Flanigan et al. (29) investigated the effects of several methods of laboratory weathering on the results of various analytical methods. They also attempted to separate the relative importance of variables such as dissolution, evaporation, photooxidation, etc. as to their effects. Dissolution and evaporation were the variables that most affected GC and IR; photooxidation most affected fluorescence.

Anderson et al. (30) have been developing a technique for weathering neat samples of suspect oils (i.e., with total absence of water) in a thin film under long-wavelength ultraviolet radiation with air passed over the surface. This technique permits convenient accelerated weathering of small samples—from approximately 1 mL in a small petri dish to 30 mg on an infrared salt plate. Under these conditions, the ultraviolet becomes an important factor in weathering, particularly in the generation of carbonyl.

Gruenfeld and Frederick (31) developed an evaporative method that can be used for samples as small as 70 mg. The sample, contained in a vial, is suspended in a 40°C water bath for 15 min in the presence of a filtered airstream. Gas chromatograms of the “weathered” sample showed that it gave virtually the same trace as a 50-mL sample distilled according to the ASTM sample preparation technique. Even more remarkable is the fact that they obtained the same trace from 0.5–30 mg of oil that had been dispersed in water and was extracted and evaporated, that is, they were able to match a sample of South Louisiana crude oil from the water column with a neat sample of oil that had been “weathered.”

Zürcher and Thüer (32), in a recent paper, examined the effects of suspended solids (kaolinite) on the weathering of a No. 2 fuel oil by GC and IR. They found that there was fractionation of the oil with alkylated benzenes and naphthalenes enriched in the water phase while aliphatic hydrocarbons (above MW 250) were adsorbed. They also found that with increased turbulence, oil droplets were agglomerated with suspended minerals. They observed the same fractionation pattern for a ground-water oil spill, despite the fact that the oil had been biochemically altered.

Infrared. The use of infrared for oil fingerprinting is well documented (32, 33, 34, 35). The technique has a well-demonstrated capability and is one of the four primary Coast Guard methods (18) that is in operational use by COIL. In addition, it has been tested in the field for over a year in Philadelphia and will shortly begin testing in San Francisco, California, and New York, using relatively inexpensive dual-beam grating instruments.

The biggest breakthrough in the medium-priced instrument field is the advent of commercially available spectrophotometers with digitizing capability. At least two of these spectrometers have software that permits curve ratioing or subtraction and other valuable routines. Digitizing in these instruments assumes a flat baseline, as was anticipated at our first pattern recognition seminar in 1975 (36). The advantages of using the horizontal baseline were subsequently demonstrated by Mattson et al. (37, 38). At this same seminar, it was decided to standardize on a horizontal baseline drawn from $1975 \pm 20 \text{ cm}^{-1}$ for oil fingerprinting. Any deviation from this line was considered to be real and meaningful. The cell window material selected was KBr with AgBr or AgCl acceptable for field use.

Commercial instruments, for the most part, read frequencies only at peak maxima that exceed specified thresholds. Unfortunately, on one instrument we found that only half of the standard 18 wavenumbers we use in pattern recognition were recorded. Furthermore, weathering shifts peak positions, which results in different wavenumbers being printed out for nominally the "same" peak, meaning that the pattern recognition was comparing absorbances at slightly different wavenumbers. To correct these problems and to get the data at the desired wavenumbers, it was necessary to interface the commercial instruments with our own designed microprocessor systems, which digitized the absorbance at prespecified wavenumbers, regardless of whether or not there were peak maxima.

In our work, although we use the 18 peaks listed in Table I, some others are digitized because they give valuable information about the sample. Three such peaks are: the 1708 cm^{-1} , which gives a quick estimate of the degree of oxidative weathering; the 1600 cm^{-1} , which gives an idea of the aromaticity; and the 1375 cm^{-1} , which, because of its little variance over the entire population of oils [Mattson et al. (37, 38)], is a ready index of thickness.

Mattson also found that the 1375-cm^{-1} peak had the largest analytical error of those peaks measured. Part of the reason is that the peak is so strong that its absorbance approaches 1 in a 0.05-mm cell and 2 in a 0.1-mm cell. According to Hannah (36), thick cells in optical null instruments give nonlinear absorbance. They are linear only up to absorbances of 0.8 to 1.0. Ratio recording systems, such as that used by Mattson, are

linear up to 1.3 absorbance units. This suggests that the thickness of 0.05 mm, as used by Brown and the Coast Guard, is best for oil fingerprinting in optical null instruments.

The availability of digitized data has led to a number of pattern recognition schemes (26, 37–41). Of these, one of the most useful is Brown's log-ratio method (26), which is adaptable to GC and other data as well as IR data. Ahmadian et al. (28) used this method to study simulated weathering. We applied the log-ratio method first to single-beam infrared data (42); then, using dual-beam infrared data, we studied the quantitative effects of weathering using a microprocessor of our own design to evaluate all 20 oils used in the previously described interlaboratory weathering study (43).

In one of our most recent applications of the Brown log-ratio method, we compensated for weathering by applying weighting factors to the data for each of the peaks, weighting most strongly those peaks that changed the least with weathering (44). The peaks we used for matching oils are shown in Table I, along with the empirically assigned weighting factors first selected and a second set labeled vector weighting factors. Both sets of weighting factors improved the results of the log-ratio method and gave clean matches of all but No. 2 fuel oils. We expect that simulated weathering of suspects will be required for optimal results with light oils.

The vector, referred to in Table I, alludes to a promising new pattern recognition technique developed by Killeen et al. (45). It uses the data from a suspect and a partially weathered sample of the suspect to estab-

Table I. Weighting Factors for 18 Peaks Used for Comparison

<i>Wavenumber</i>	<i>Empirical</i>	<i>Vector</i>
1304	0.8	0.9
1165	0.5	0.3
1145	0.3	0.3
1070	0.3	0.3
1032	0.5	0.3
955	0.6	0.9
918	0.7	0.9
890	1.0	0.9
871	0.9	0.9
849	1.0	0.9
832	1.0	0.9
810	0.4	0.4
790	0.5	0.9
782	0.4	0.4
766	0.5	0.9
744	0.7	0.4
722	0.6	0.4
700	0.4	0.4

lish the direction of change for each data point, actually generating an 18-dimensional hyperplane. The spill is then compared with the closest fit to that plane, the closest fit being called the "computer-simulated weathering" data for the suspect. An example of a computer plot for a spilled No. 4 fuel oil is shown in Figure 2, along with the plot of the suspect, which has a significantly different trace. However, the computer-simulated plot for the suspect can be seen to be a virtual overlay to the spill, including a crossover of both at about 980 cm^{-1} . When two different No. 4 fuel oils were compared by the vector method, the simulated weathering curve from one actually diverged from the other, that is, the method does not make all oils look more alike. An illustration with a No. 6 fuel oil can be seen in Ref. 24.

In a second part of the report on the interlaboratory weathering study (25), different pattern recognition techniques were evaluated using the Mann-Whitney U -statistic (46). For each of the four oil types 15 pairwise comparisons were made quantitatively, and the results were serially ranked according to the closeness of match. An example is given below for only 5 pairwise comparisons. After ranking the oils sequentially, their identities are tabulated as to whether or not they are the same (S) or different (D) from the known oils that were analyzed in the interlaboratory study. Ideally, all of the weathered oils from a common source should be grouped together, as shown in Table II. In the actual case, this is not true. The U -statistic is determined by counting how

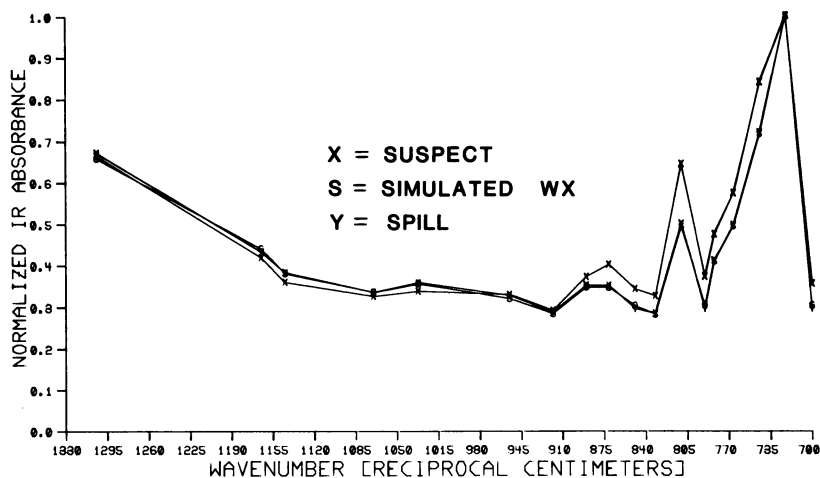


Figure 2. Computer printout of connected data points from a spilled No. 4 fuel oil and a suspect. It also shows the computer-simulated weathering data for the suspect as a near overlay for the spill.

Table II. Illustration of Mann–Whitney U-Statistic

	<i>Rank</i>					
	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>Score</i>
Ideal	<i>S</i>	<i>S</i>	<i>S</i>	<i>D</i>	<i>D</i>	0
Actual	<i>S</i>	<i>S</i>	<i>D</i>	<i>S</i>	<i>D</i>	1

many times an *S* is separated by a *D* from the other *S*'s; that is, each time an *S* must pass a *D* to join the other *S*'s, the *U*-statistic is incremented by one. In the actual case illustrated, the *S*-ranked No. 4 must pass one *D* at rank 3 and the *U*-value is therefore 1.

With 15 comparisons involving six pairs of *S*'s and nine pairs of *D*'s unweathered oils, the maximum *U*-value would be 54; the value for random ranking would be 27. The better pattern recognition schemes gave values of 0–5; that is, the lower the number generated, the better the method was in making oil comparisons. (*Note:* The random chance of getting a numerical value of less than 6 is 0.4%.)

The evaluation involved four basic methods and variants of them. They included: the standard visual overlay method, or a modification of it that involved some linear measurements in the fingerprint region of the infrared spectrum; the Brown log-ratio method (26); the vector method devised by Killeen et al. (44, 45); and the standard ASTM method (22). The overlay method was the best method when used by someone experienced in interpreting weathered oils.

The quantitative methods required digitization of 18 peaks (*see* Table I), either manually or electronically. The log-ratio method was evaluated using an average percent difference value for the 18 peaks, or alternatively the Brown S^2 statistic (26), which seemed a better measure of the validity of the method. The log-ratio method was also evaluated using a variety of weighting factors for each peak (*see* previous discussion). The vector method and log-ratio methods were both significantly improved by artificially weathering suspects prior to comparison with spill samples. Further work is being conducted in this area. The primary conclusion is that for quantitative comparisons, an artificial weathering of suspects is needed for optimum results.

Grizzle and Coleman (34, 35) recently reported an extensive study on crude oils. Although its results are internally consistent, some practices are not recommended for routine oil spill fingerprinting. They are:

1. *The Use of Distillation as an Artificial Weathering with a 10-mL Sample.* There is nothing inherently wrong with this approach. It closely parallels the standard ASTM D3326 procedure. The problem arises from the fact that in real world situations actual samples may be 1 mL or less.

2. *The Use of Sodium Chloride Cells.* This is perfectly acceptable when comparing to other NaCl spectra. However, Brown (26) showed that KBr and AgCl gave better results and could be compared with each other but not with NaCl. The consensus (36) was that KBr is the recommended window material.
3. *The Use of 0.1-mm Cells.* For routine use, we recommend the 0.05-mm sealed-demountable cells because some of their absorbances in 0.1-mm cells are in the nonlinear range for optical null instruments and the standard deviations rise significantly. Furthermore, a single sealed cell changes with continued use, particularly when some intractable spill samples may have traces of residual water. We have demonstrated that triplicate analyses of a No. 2 fuel oil show not even line width variations in a properly used sealed-demountable cell.
4. *The Use of a Straight Percent Difference Calculation.* The method used by Grizzle and Coleman again was satisfactory for their purposes. It lacks two properties of the Brown logarithmic method, which make the latter much better suited for routine oil comparisons. First, the Brown equation cancels out thickness dependence. This not only includes variations within a given cell but also, and more importantly, permits comparison with any oil in the data file analyzed at any time in any cell. The second, and still more important, distinction for anyone comparing oils in data files is the fact that the Brown method, by using logs, makes it immaterial how the oils are compared, $X:Y$ or $Y:X$. This is not true of the Grizzle-Coleman equation, which compares absorbances A at the i th frequency for two oils, X and Y :

$$\left(\frac{A_i^X}{A_i^Y} - 1.0 \right) 100 = \% \text{ difference}$$

From this equation, it can be seen that the ratio and its reciprocal would give different answers, conceivably indicating a match when compared one way and a nonmatch when compared the other way.

Despite the refinements yet to be made with the use of infrared fingerprinting of oils, there is no doubt that it is one of the better methods.

Gas Chromatography. Gas chromatography is one of the "work-horse" methods used for oil identification. The newly approved ATSM Method D3328-78 (4) incorporates simultaneous flame photometric detection along with flame ionization detection. Such dual detection, using a high-resolution SCOT column is the routine method employed by COIL for Coast Guard analyses.

Since the last review by this author (1,2), an early paper in this field came to light in which Johnson and Fulmer (47) used three detectors simultaneously—FID, and FPD for both sulfur and phosphorus. The phosphorus FPD was considered especially useful for detecting the presence of contaminants of biological origin, such as vegetable oils.

The thermionic nitrogen–phosphorus detector (NPD) was employed by Lee et al. (48), using an SE-52 SCOT column for fingerprinting used engine oils for forensic purposes. Nitromethane extracts containing the polynuclear hydrocarbon fraction yielded peak patterns with either an FID or NPD, which were characteristic for a particular engine.

Meanwhile, Flanigan and Frame (49) successfully applied a commercially available NPD with an independently heated rubidium bead to fingerprint petroleum and synthetic oils. They found that FID, used simultaneously with the NPD, was useful to assess NPD response to the large excess of nonnitrogen-containing hydrocarbons coeluting with the nitrogenous compounds. They also demonstrated that the NPD-active nitrogen compounds could be concentrated and isolated from the majority of interfering hydrocarbons by the use of an alumina chromatographic column. The hydrocarbons were first eluted with a nonpolar solvent, followed by a more polar solvent to remove the sample of interest.

Frame et al. (50) have published an atlas of over 70 dual FID/NPD chromatograms of a wide variety of oils separated on a 15.2-m Dexsil 300 SCOT column. They note that the NPD fingerprints of light oils may be lost after weathering, but that those of spilled heavy crudes and residual oils are very stable. For example, they were able to match the NPD peak pattern of an open ocean oil slick sample to the *Argo Merchant* cargo after the slick had been on the water for three weeks.

Kawahara (51) found that he could identify spilled asphalts by making the pentafluorobenzyl thioethers and ethers from traces of mercaptans and phenols in asphalts, and separating them by gas chromatography, using an electron capture detector to obtain the distinctive chromatograms.

Rasmussen (52) used a 30.4-m Dexsil 300 SCOT column (compared with the 15.2-m used by COIL) to obtain high-resolution separations. He then numbered the minor peaks between the *n*-alkane peaks and expressed the areas of each of these as a percentage of the preceding *n*-alkane. For each alkane peak, strings of numbers were generated that could be compared between oils for identification, particularly those above C₁₄.

Another use of SCOT SE-52 columns was reported by Cverton et al. (53), in which a glass capillary 35 m long was coated with SE-52 to obtain sufficiently high resolution to perceive crude oil pollution among sediment

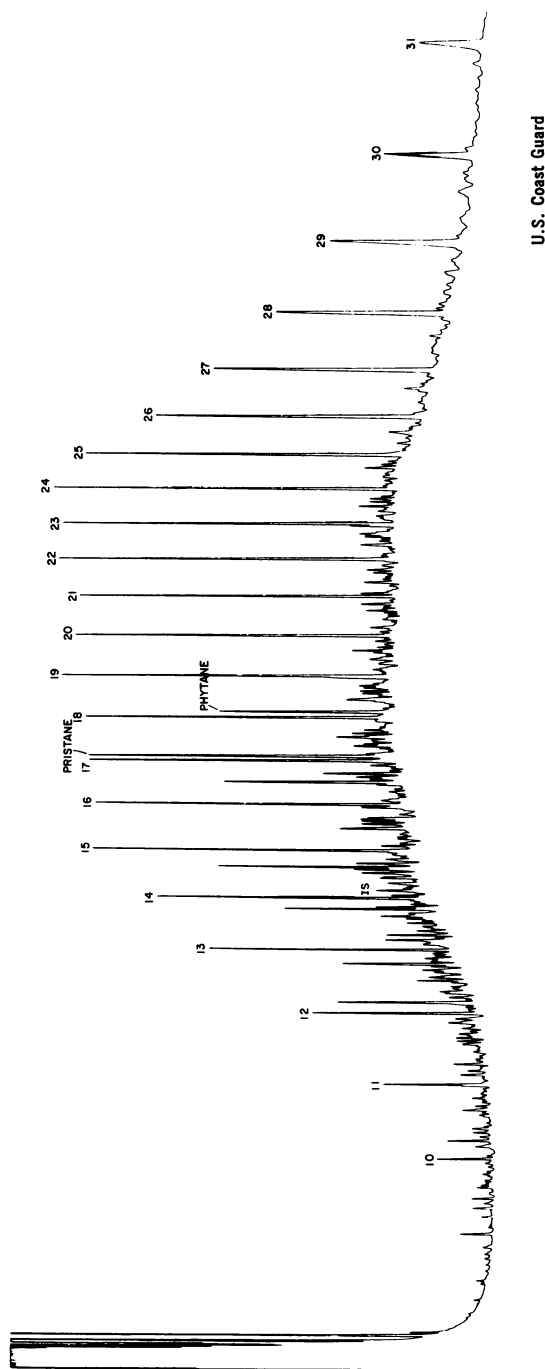
hydrocarbons. The authors feel that glass capillaries offer an answer to the difficult problem of distinguishing petroleum-type hydrocarbons in the marine environment from hydrocarbons of recent biogenic origin.

MacLeod et al. (54, 55) have found the high resolution achieved by glass capillaries to be extremely useful in identifying the source of oil pollution in marine biota. Two-meter capillaries with rapid temperature programming were excellent for screening, since they could analyze C_{10} – C_{34} hydrocarbons in 7 min vs. 40 min for a 2-m packed column of comparable resolution. High-resolution separations were achieved with a 20-m capillary column. The saturated and aromatic hydrocarbon fractions were separated on a silica gel column first and analyzed separately by capillary GC. Horizontal scale expansion showed 15–40 discrete hydrocarbon components in the intervals between adjacent *n*-alkane peaks; these were found useful in determining the identity of the source oil.

Figure 3 shows the separation achieved of the saturated hydrocarbons from the stomach contents of cod near the *Argo Merchant* oil slick. These were virtually identical to saturated hydrocarbons in the *Argo Merchant* cargo. These samples were obtained from homogenized tissue that was digested with alkali, solvent extracted, and chromatographed on silica gel. The GC analysis was carried out on a 20-m glass capillary of 0.25-mm i.d., coated with 0.5- μ m film of SE-30. A 0.2- μ L sample was injected (splitless for 12 sec, then split 10:1 with 14 psig He carrier). The temperature was isothermal at 40°C for 5 min, then programmed to 270°C at 4°C/min. The findings showed that the stomach contents of cod collected at a particular location undeniably had been contaminated with *Argo Merchant* oil. There were indications that windowpane flounder may have ingested some of the oil, based on the saturated hydrocarbon profile, but the aromatics were too low for comparison.

MacLeod et al. (56) made use of their capillary technique to make weathering estimations for spilled oil from the barge *Bouchard No. 65* (Buzzard's Bay, Massachusetts, January 1977). This was accomplished by obtaining peak areas for the *n*-alkanes, C_9 – C_{22} , plus pristane and phytane in the aliphatic fraction and for 21 arenes among the aromatics. The alkanes were normalized to C_{17} ; the arenes to phenanthrene. From these numbers, the percentage loss of each was computed, and the overall oil losses were estimated by taking a weighted average of the alkene and arene loss estimates. The arenes exhibited greater percentage losses than the alkanes (as much as 89% despite the frigid conditions of the spill). The losses generally correlated with exposure to the atmosphere.

In a study reported at the 1977 Pittsburgh Conference (57), we examined quantitative changes in gas chromatograms for different oil types weathered over four days. All peak heights were normalized to C_{20} on the supposition that the C_{20} peak would be stable. However, even C_{20}



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Figure 3. Glass capillary gas chromatogram (high resolution) of saturated hydrocarbons from stomach contents of cod near the Argo Merchant oil slick, which is virtually identical to saturated hydrocarbons in Argo Merchant cargo oil. Numerals denote n-alkane chain length (55).

showed some loss in No. 2 fuel oil. The peak heights were found generally to diminish logarithmically. A semilog plot of normalized peak heights vs. days of weathering gave a straight line of steep slope for C_{12} and lesser slopes for C_{13} and C_{14} . From C_{15} upward, the lines were nearly horizontal, with some slight discontinuities between Day 0 and Day 1 weathering. The lines were given by the expression

$$Z = Z_0 e^{mt}$$

where Z = peak height, Z_0 = intercept, m = slope, and t = weathering time (days).

This equation suggested that once the slope and intercept are known for a given oil type, a peak height measurement could be used to estimate the weathering time in days. This calculation was made for a No. 2 fuel oil as shown in Table III. These data seem to indicate that under certain circumstances, some rough estimates of weathering time might be possible, but the problem would require further study for this assumption to be made generally applicable.

Other conclusions of the quantitative study were that sample preparation is very important and samples being compared should be analyzed under identical conditions—preferably on the same day. Best matching was achieved if suspects were subjected to accelerated weathering before analysis. The Brown log-ratio (26) was found applicable and was used to demonstrate that a good range of hydrocarbons to use (one which is relatively insensitive to weathering) is C_{16} – C_{22} , including pristane and phytane peaks.

Fluorescence. The fluorescence spectroscopic (FL) method approved by ASTM (5) is similar in most respects to that used by the Coast Guard. Unless the samples are collected soon after the spill occurs, it is not recommended for volatile fuels such as gasoline, kerosene, and No. 1 fuel oils because of their rapid changes with weathering. Some No. 2 fuel oils and light crude oils may be identifiable with only up to one or two days of weathering.

Table III. Calculated Weathering Time from C_{12} and C_{14} Peak Heights

<i>Actual Days</i>	C_{12}	C_{14}
1	0.91	1.42
2	1.78	2.52
3	2.99	3.50
4	3.97	4.02

Fluorescence applied to oil identification has been an active field, with 17 papers presented on the subject at the last three Pittsburgh Conferences. A number of interesting developments for fluorescence and low-temperature luminescence (LTL) are described by Eastwood et al. (58). These include synchronous scanning, difference spectrofluorometry, synchronous difference spectroscopy, derivative spectroscopy, and total luminescence (or contour) spectroscopy and combinations of these techniques. In a recent presentation, Eastwood and Hendrick (59) reported an extension of their low-temperature luminescence studies to include polarized excitation and emission spectroscopy, and time-resolved phosphorescence. Preliminary studies of polarization effects indicate that differences exist in low-temperature polarized luminescence spectra of oils, which may aid in oil identification. In the time-resolved phosphorescence spectra of oils, the most significant difference observed was enhancement of the vanadyl porphyrin signal at approximately 700 nm for short delay times (20 μ sec).

Fortier and Eastwood (60) reported on the use of low-temperature luminescence to achieve more structure than room temperature fluorescence spectra for fuel oils, thereby enhancing oil-matching capabilities. Eastwood et al. (61) conducted FL and LTL studies on weathered oils. They tested corrected emission spectra at room temperature and at 77 K (20 ppm oil in methylcyclohexane) using excitations at 254, 290, and 330 nm; synchronous scanning, with a 25-nm wavelength offset between excitation and emission to obtain additional structure; and difference spectra (dual-beam) for direct comparison of changes due to weathering. Matching capabilities usually appeared to be satisfactory for up to one week of weathering for heavy oils and up to two days of weathering for light oils.

Another recent paper showing the advantage of synchronous scanning over conventional fluorescence emission, as applied to geochemistry, is that of Wakeham (62). He found that greater information on the aromatic content of oils could be obtained by separating the aromatic hydrocarbon fractions by liquid-solid column chromatography prior to fluorescence analysis. He was able to distinguish indigenous and petroleum hydrocarbons found in sediments of Lake Washington.

With the advent of computerized systems and readily available hardware, total luminescence is gaining adherents. Brownrigg and Hornig (63) and Hornig and Giering (64) have reported on the low-temperature total luminescence applied to weather oils. Warner et al. (65) at the University of Washington applied sophisticated pattern recognition techniques to resolve a model mixture of nine petroleum-type polynuclear aromatic compounds from the complex total luminescence emission-excitation matrix (EEM).

From the same University of Washington group, Johnson et al. (66) reported rapid scanning fluorescence spectroscopy based on a "novel" scheme for polychromatic irradiation of the sample cuvette and the use of a silicon-intensified target (SIT) vidicon detector to measure all regions of the EEM simultaneously. The computer-controlled instrument, patented in 1977 by Callis and Davidson (67) is capable of acquiring an EEM spanning up to 240 nm in emission and excitation wavelengths at a spatial resolution of 1 nm per point in a time as short as 16.7 msec. The instrument shows promise for improving multicomponent capabilities of fluorescence assays, at some cost in sensitivity. One major disadvantage is that for absolute spectroscopy each of the resolution elements must be calibrated individually, but only a few matrix locations may suffice for certain types of analysis.

Independently, Jadamec et al. (68) developed a similar system for continuous real-time acquisition of fluorescence emission spectra of eluting petroleum oil fractions separated by high-pressure liquid chromatography. Using an optical multichannel analyzer detector, which has a spectral response over the range of 190 to 900 nm, the spectral window between 290 to 400 nm was examined (0.2 nm per channel) with a complete frame scan of the detector target every 31 msec. This system too prints out quasi-three-dimensional displays in numerous formats. Its value lies in the fact that the short scan times permit assessment of eluting peak homogeneity and identification of the compounds present in pure fractions. The prototype instrument designed by this group will soon be modified to permit simultaneous analysis by ultraviolet absorption spectra for those compounds that do not fluoresce.

The University of Washington group, Christian et al. (69), recently introduced a unique micro-flow-through cell for fluorescence determination of effluents from liquid chromatography columns. A laminar flow design reduces scatter and minimizes dead volume. The sample volume can be maintained at less than 100 nL with a wide range of flow rates.

Miscellaneous Methods for Oil Identification. High-pressure liquid chromatography has already been mentioned in conjunction with rapid fluorescence detection. It fully characterizes the polar fractions containing the polynuclear aromatic hydrocarbons and could be of use in those cases where their overall fluorescence fingerprint cannot distinguish between two oils.

Saner et al. (70) report on the use of reverse-phase liquid chromatography for the identification of oils using dual ultraviolet absorption detection (210 and 254 nm). During these studies, Saner et al. (71) showed that temperatures elevated to 60°C diminished resolution for 5- μ m-diameter particles (both C₈ and C₁₈) but increased resolution for 10- μ m-diameter C₁₈ reverse-phase columns.

In the most recent edition of *Chromatography* by Heftman (72), 11 references from the early 1970s are cited in which gel permeation chromatography (GPC) is used for either the examination of high-molecular-weight petroleum fractions or the "identification of crude oils, etc., by 'fingerprint' comparison."

Saner and Fitzgerald (73) reported a method for thin-layer chromatographic identification of oils that was the basis for the current Coast Guard TLC method employed by COIL and FOIL.

Hendrick and Eastwood (74) recently reexamined the use of vanadium and nickel concentrations and V:Ni ratios as a means of identifying weathered oils, because of the reputed stability of the ratios. They used a DC argon plasma emission echelle spectrometer equipped with a microprocessor. A statistically designed experiment (two-level factorial) showed that there was no enhancement effect of sodium in the concentration ranges of interest. These workers showed that the plasma emission method was applicable to heavy crude and fuel oils even after several days of weathering with as little as a half a gram of sample when the oil has a concentration of at least 20 ppm of V and Ni. The sample is analyzed merely by diluting with spectroquality xylene (no ashing or sample pretreatment required). For lighter oils where metal ion concentrations are lower, and where larger samples of weathered oils are not available, the method is less useful. This was a preliminary evaluation and not all instrument parameters were fully optimized.

Finally, an interesting new approach using computerized gas chromatography-mass spectrometry (GC-MS) is being developed by Flory et al. (75) and Koons et al. (76). The technique involves analysis of selected fractions with their fingerprints plotted by computer. Specific ions indicative of indigenous biological markers have been monitored. Two series of biological markers chosen were the C₁₅₊ alkane series and their corresponding isoprenoids, and the steroid- and triterpenoid-type hydrocarbons (the C₂₇₊ cyclics). For the two groups, *m/e* 191 (five-ring naphthenes or triterpanes) and 217, four-ring naphthenes (steranes), respectively, were monitored and the computer enhanced the data by subtracting background to produce a reconstructed gas chromatogram from each. The mass chromatograms thus plotted serve as specific indicators for the isoprenoid and cyclic compounds, provide resolution of compounds not completely separated by the GC column, and greatly increase the dynamic range. These workers believe that this technique will substantially improve the potential for classifying oils over other currently used methods.

Remote Sensing

The growing worldwide concern over pollution of our finite planet has led to increased international interest in remote sensing. An example

of this is current interest of the European Economic Community in satellite surveillance of the Mediterranean for pollution (77). Applications abound as more sophisticated hardware becomes available. Twelve international symposia have been held on remote sensing of the environment with voluminous proceedings attesting to the extent of ongoing research.

Although the term "remote sensing" includes sensing from satellites, the Coast Guard originally perceived airborne surveillance and local area surveillance as the two most practical approaches to satisfy its needs. Local area surveillance, as the name implies, involves monitoring harbors and waterways that are more or less confined. Airborne surveillance is the approach used for wide area coverage of open sea.

The Federal Water Pollution Control Act (Public Law 80-845) prohibits "discharges of oil into or upon the navigable waters of the United States." The International Convention for the Prevention of Pollution at Sea by Oil (1954), which was ratified by the U.S. Senate as the Oil Pollution Control Act in 1961, prohibited tankers from discharging oily mixtures within at least 50 miles of land. Today, the prohibited discharge zone extends to 200 nautical miles. This means that the surveillance of the 4500 miles of contiguous U.S. coastline must provide regular coverage of 900,000 square miles of ocean (78). The amount of ocean to be covered necessitates much more emphasis on airborne surveillance. The EPA has similar responsibilities under the law; Melfi et al. (79) recently reviewed the EPA needs in remote sensing.

The literature on the subject of remote sensing began to grow significantly in the late 1960s for all applications. Every conceivable technique seems to have been tried for feasibility for oil identification. Some of these include infrared reflectance sensors [in which the signals at two wavelengths in the 3- μ m region are ratioed (80)], an active fluorosensor system (81), a laser backscatter sensor called a Dichromatic Lidar Polarimeter [LIDAR for light detection and ranging—see also Rause et al. (82)] that uses 632-nm red and 442-nm blue lasers and measures horizontally and vertically polarized backscattered light, laser Raman (83), and vapor sensors based on (a) a coated piezoelectric crystal, (b) a semiconductor gas sensor (Taguchi Gas Sensor or TGS), (c) a vapor absorption/resistor sensor, and (d) a differential evaporation sensor based on differential evaporation rates on water and oil-coated temperature probes.

Several of the sensors mentioned above were evaluated by the U.S. Coast Guard [White and Arecchi (84)] for use in local area pollution surveillance systems in various ports and estuarine areas. They were tested for their ability to give early alerts to spills, which would permit prompt containment and cleanup efforts and thereby minimize

environmental damage. All those tested had limited capabilities in one aspect or another for local pollution surveillance. Three promising sensors were put through field tests for six months in New York Harbor. White (85) encountered operational difficulties involving thin-film sensitivity, threshold levels in the presence of background oil films, and alarm time delays. He felt these types of sensors would be more effective monitoring specific problem areas such as moored tankers and storm drain outfalls. One of the most difficult problems with point sensors is determining the placement location. Bacon (86) addressed this from the oceanographic point of view in Providence Harbor, Rhode Island. Spill movement models were used to estimate movement patterns, which were transferred to a map grid to estimate the number of spills that might occur in a given grid space. For precise location of sensors, a very detailed study would be required of currents on a small scale.

Preliminary studies for airborne systems were reported by Meeks et al. (87), who studied microwave radiometric detection of oil slicks. A couple of years later, Fantasia and Ingrao (88) and Ingrao et al. (89) described the development of an experimental airborne remote sensing system for oil spills, based on laser-stimulated oil fluorescence. At the Tenth International Symposium on Remote Sensing, in 1975, several techniques were reported, including a passive infrared (90), radar observation of spills (91), passive luminescence with a Fraunhofer line discriminator (FLD) (92), and active luminescence (93) and fluorescence (94).

Two groups are pursuing the use of active fluorescence. They are the Canada Centre for Remote Sensing and NASA Wallops Flight Center. Both have studied extensively spectral and temporal identification of oils (95, 96, 97). Time-resolved spectra are possible since the red portion takes longer to decay than the blue portion of the spectrum; by gating, a time-delayed spectrum can be obtained with a temporal resolution of 5–10 nsec. The Canadian group has reported on a laboratory study of time-resolved fluorosensors for remote characterization of oils (98). Both the Canadian and NASA groups have decided, for the present, to concentrate on active fluorescence using a single narrow laser pulse with a spectrometer receiver tuned to multichannels to obtain a real-time total fluorescence spectrum. The Canadians use a 16-channel receiver in their operational active fluorosensor. NASA uses a 40-channel receiver with a spectral resolution of 11.25 nm/channel in the measured range of 350–800 nm, using a laser tuned to 337 nm. Both groups are awaiting spills of opportunity for real world testing.

Radar observations of spills have already been mentioned (91). A synthetic aperture radar on board *Seasat A* will be used with a 16-ft vertically polarized antenna to look at natural seeps over Santa Barbara

Channel and Baffin Bay (99) after studying icebergs off Newfoundland.

The Coast Guard's Airborne Surveillance System (AOSS) has been very successful, so much so that it is now entering its third generation. In 1972 Catoe (100) presented a state-of-the-art survey that contained elements of the AOSS predecessors. The current system being used is AOSS II (78, 101, 102). Edgerton et al. (103, 104) described the prototype of the AOSS system, which is a multisensor system that provides real-time, day or night, all-weather detection, mapping, and documentation of oil spills at sea. The prototype system was installed on a Coast Guard HU-16 Albatross aircraft and tested off the California coast with natural oil seeps, routine shipping, and targets of opportunity. The system consisted of a side-looking radar, a passive microwave imager, a multispectral low-light-level TV, a multichannel line scanner, a position reference system, and a real-time processor/display console.

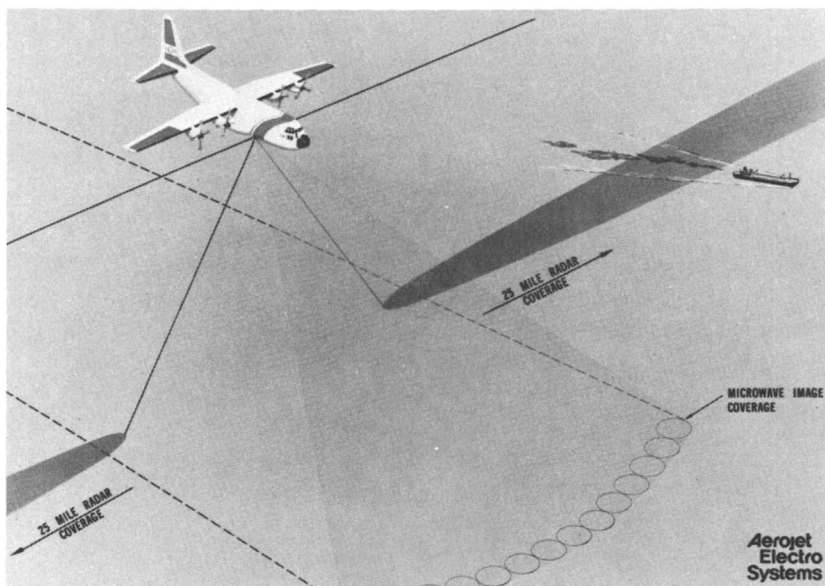
The AOSS I flight evaluations were reported by Mauer and Edgerton (105), and the entire system reviewed by Woolever et al. (101). The planned phasing out of the Coast Guard's Albatross fleet, coupled with required improvements in the AOSS I system, led to installation of an improved system, designated AOSS II in the U.S. Coast Guard HC-130B aircraft (106).

The major subsystems of the AOSS II include the following improvements:

1. Double-sided SLAR antenna installation for left/right detection and mapping capability.
2. Increased microwave scanner rotation speed to permit lower-altitude operations and higher resolution.
3. Installation of an improved aerial reconnaissance camera (KS-72) in lieu of the low-light-level television.
4. Use of IR line scanner to provide printout of surface water temperature along the flight track.
5. Expanded hard-copy recording capability, computerized target latitude/longitude readout, and image smoothing at the operator's display console.

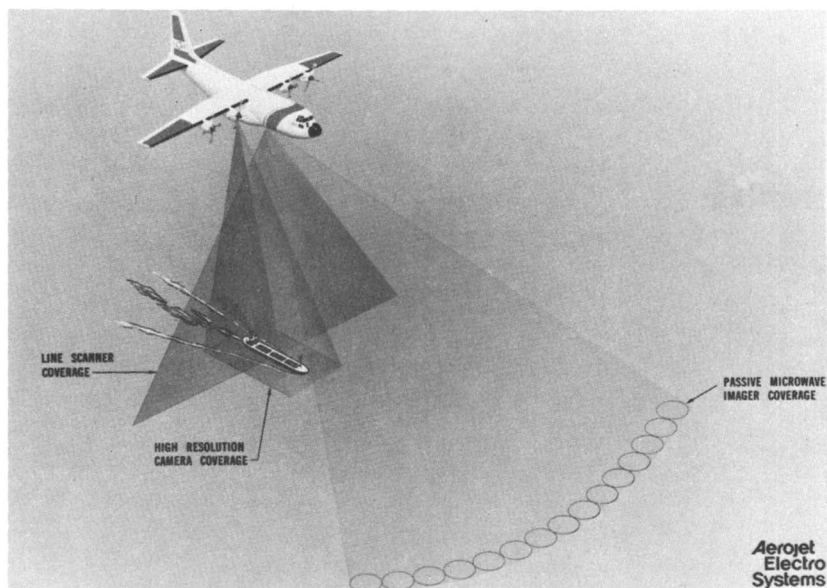
AOSS II became operational in April 1977 and has increased the surveillance productivity over that of the standard HC-130B aircraft fourfold. According to White et al. (102), "Never before in Coast Guard history has a single aircraft imaged as much territory in as short a time."

The AOSS II integrated multisensor system provides effective surveillance around the clock and under all but extreme weather conditions. Figure 4 illustrates how the passive microwave imager and side-looking radar system provide long-range surveillance—up to 25 miles on either side of the aircraft. Figure 5 shows how the system employs the reconnaissance camera and multichannel line scanner for high-resolution documentation of oily discharges and suspected violators.



U.S. Coast Guard

Figure 4. AOSS II long-range ship/discharge detection and mapping mode (106)



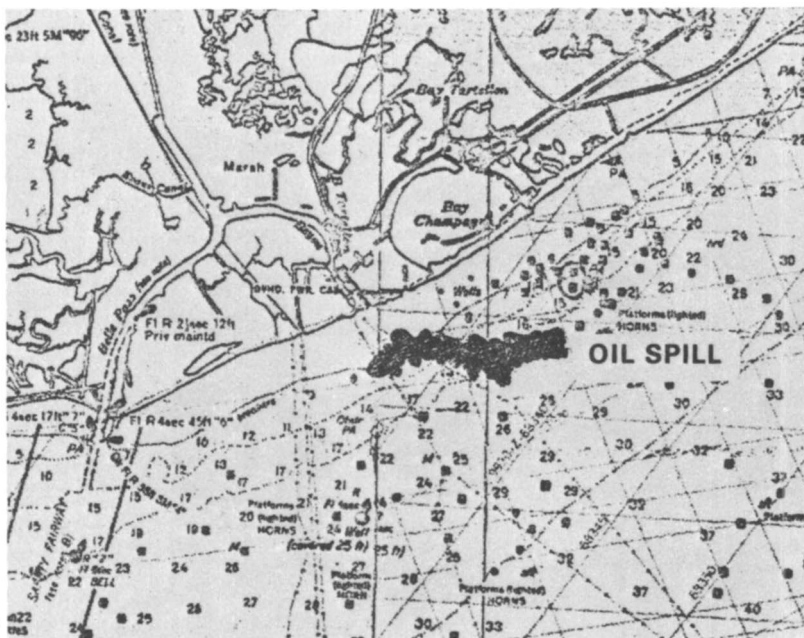
U.S. Coast Guard

Figure 5. AOSS II short-range inspection/identification and mapping mode (106)

The side-looking radar mapping system utilizes a unique 8-ft vertically polarized antenna for oil detection and mapping. A standard 16-ft antenna complements the 8-ft antenna to provide a 50-nautical mile swath width, and digital filters are employed for automated target detection. This system produces a near-real-time radar map on film that can be sent to a ground station while the aircraft continues its patrol. Figure 6 shows the outline of a spill superimposed on a chart as it is received on the ground. It shows the location and extent of the slick, so that ground response teams can take appropriate action.

The inertial navigation system and airborne data annotation system of AOSS II provide position references that are superimposed on all data products. The four sensors and position reference system are integrated by means of a software-controlled operator console that requires only one operator. Color and black-and-white TV monitors display information from the sensors. Under low-contrast conditions, false color enhancement is used to facilitate interpretation.

The third generation, called AIREYE (from the acronym ARI, which stands for Airborne Remote Instrumentation) is on the drawing boards to be installed in Falcon 20G jet aircraft starting in mid-1979. This will



U.S. Coast Guard

Figure 6. Outline of spill superimposed on chart as it is received on the ground

replace the HU-16E Albatross and will be designated the HU-25A. It will serve as the Coast Guard's Medium Range Surveillance (MRS) aircraft. The AIREYE system is based on the AOSS II system but will be smaller in size (2.25 m^3 vs. 3.75 m^3) and weight (one-third the weight of the AOSS II package). There will be improvements in all components of the system. The components will consist of side-looking radar (SLAR), an infrared/ultraviolet line scanner (IR/UV), an aerial reconnaissance camera (KS-87B), an airborne data annotation system (AN/ASQ-154), and an active gated television (AGTV) and a control display and record console (CDRC). Figure 7 shows the location of the AIREYE sensors on the aircraft.

The AIREYE SLAR will have a 200-kW transmitter vs. 45 kW in AOSS. It will also have a dry film silver radar processor instead of a wet chemical processor. It will be the primary oil pollution detection sensor, detecting slicks by reduction of ocean clutter from 2–25 miles on both sides of the aircraft and providing a near-real-time annotated map.

The IR/UV line scanner is the same as AOSS, except the UV sensitivity will be increased by a factor of 10. The IR/UV will scan a line missed by the SLAR. It can differentiate between oil and false targets and is effective in calm water when SLAR is degraded. The IR portion provides a day or night capability.

The KS-87B camera is in the Department of Defense inventory. It is a pulse-operated frame camera with a high-speed focal plane shutter, integral automatic exposure control and data recording, and forward

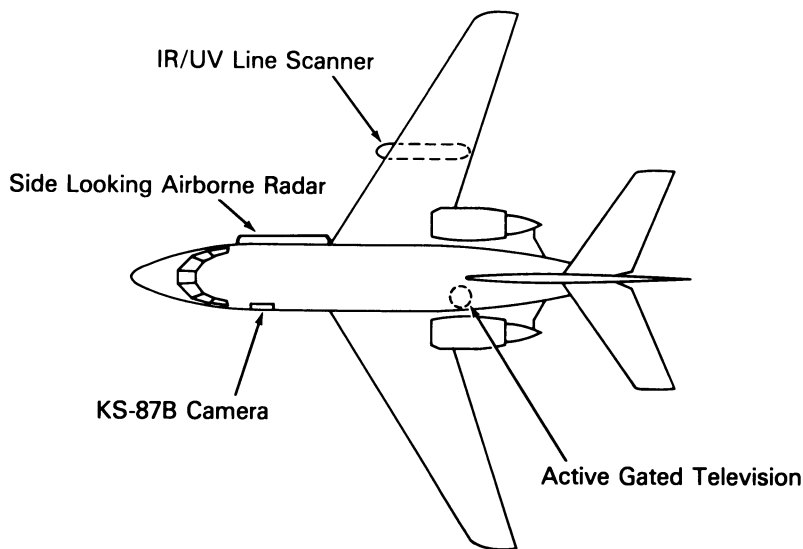


Figure 7. AIREYE sensor locations on the HU-25A (78)

motion compensated. It provides documentary evidence (ship identification) and can be operated by the pilot as well as the sensor operator.

The data system (AN/ASQ-154) is also in the Department of Defense inventory.

The AGTV is a capability the earlier AOSS II system did not have and will provide the ability to identify discharging vessels at night. It has a pulsed laser illuminator that will permit reading painted letters at night on the bow or stern of vessels and provide absolute identification for forensic purposes. This is possible because of an annotated videotape record that has a playback and freeze-frame capability to ensure the evidence is readable while the aircraft is still on scene.

The CDRC will have only one black-and-white multipurpose display in the console as a result of space limitations. However, it will provide a limited map display capability.

In its operational form, AIREYE will detect oil pollution at sea, identify violators, and provide permanent records suitable for prosecution of polluters.

Summary

The chapter presents some of the significant recent developments and indicates the direction of future developments in oil spill fingerprinting and remote sensing. Widespread adoption of uniform practices in oil identification will benefit all who are concerned with the problem of identifying sources of oil pollution. Airborne remote sensing is, at present, the only practical way to maintain pollution surveillance over wide areas of open sea.

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