Mystery Oil: Who Spilled It?

The work of the U. S. Coast Guard Marine Safety Laboratory.

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Coast Guard field investigators frequently respond to "mystery spills," oil in the environment from no obvious source, to protect the environment from further damage and to identify the source of the spill. Their physical investigation of the scene is crucial to solving the case. One of their normal tasks is to obtain samples of the spill and samples from potential sources. These samples are subjected to forensic chemical analysis in an attempt to determine the responsible party.

Figure 1: The USCG Marine Safety Laboratory in Groton, Conn., plays an intricate part in the incrimination of environmental polluters by giving U.S Attorneys physical evidence in a court trial. Chemists at the lab are expected to testify in court about the findings in the laboratory. None of the findings from the lab have ever been refuted. All procedures are checked and double-checked for accuracy. PA3 Kelly Newlin, USCG.

The Marine Safety Laboratory (MSL) is the U. S. Coast Guard's forensic laboratory for oil spill source identification. The primary function of MSL is to conduct the chemical analyses necessary to identify the source of an oil spill in support of CG investigations. MSL exists to support field investigators and various federal, state, and local agencies by providing forensic analysis of oil samples and suspected source samples. MSL works closely with the National Pollution Fund Center and the Department of Justice in the prosecution of responsible parties (Figure 1). The analytical evidence produced by MSL provides both law enforcement and cost-recovery benefits, as MSL chemists provide expert witness testimony for hearings and court proceedings as needed.

The Marine Safety Laboratory

MSL analysis is intended to serve as a powerful tool to aid Coast Guard pollution investigators in determining the source of mystery oil spills as mandated by federal law. The lab uses several complementary chemical tests that exploit the intrinsic properties of petroleum oil and make it possible to match spilled oil with its chemical source (Figure 2). MSL analysis provides the means to ascertain the responsibility for oil pollution; assess penalties; and help recover federal pollution cleanup funds expended during an incident; and serves as a deterrent to deliberate

oil pollution discharges. It is implicit that this deterrent factor will also encourage the reporting and acceptance of responsibility for accidental spills.

In addition to its primary mission, MSL is tasked to:

- Provide consultation to field investigators, District offices, hearing officers, National Pollution Fund Center, Department of Justice, and other federal agencies concerning the Oil Identification System and MSL analysis reports.
- Provide expert opinions and testimony at legal proceedings as required.
- Maintain a system of adequate quality controls to assure the integrity of the Oil Identification System.
- Evaluate new methods and advancements in technology that may increase the accuracy, reliability, and efficiency of the Oil Identification System.
- Participate in activities that enhance the credibility and legal acceptance of MSL analyses, including membership in the American Society for Testing and Materials (ASTM).
- Provide long-term secure storage of oil samples (i.e., evidence) that MSL has received from field units in support of oil pollution cases.

Figure 2: USCG Marine Safety Laboratory analysis is intended to serve as a powerful tool to aid Coast Guard pollution investigators in determining the source of mystery oil spills as mandated by federal law. PA3 Kelly Newlin, USCG.

Background, History of the Laboratory

In 1972, the Federal Water Pollution Control Act (FWPCA) assigned general responsibilities to the Coast Guard for the protection of the marine environment in the United States, including enforcement of the nation's anti-pollution discharge laws and regulations. To carry out these responsibilities, it became necessary to develop a system to identify pollutant sources. The Coast Guard Research and Development Center was tasked with this project in 1973. Over the next four years many analytical tests and procedures were evaluated for their ability to distinguish among all types of petroleum oil. In 1977, the R&D Center published its final report in the National Technical Information System (NTIS) detailing the "Coast Guard's Oil Spill Identification System." The Central Oil Identification Laboratory (COIL) was established in November 1977 to implement the system and was located within the R & D Center facilities in Groton, Conn.

One of the first steps for COIL and the new Oil Identification System was to set legal precedent for its "oil fingerprinting" technique. This occurred in December of 1978 at a federal criminal jury trial, under the Federal Water Pollution Control Act, involving spilled oil. In this case, *U.S. vs. Distler*, Judge Charles M. Allen ruled that "chemical evidence" would be admissible, thereby establishing the necessary legal precedent.

In 1979 administrative control of COIL was transferred to the Coast Guard Oceanographic Unit in Washington, D.C., and a new lab was constructed from existing Oceanographic Unit space at the Washington Navy Yard Annex. However, COIL operations under the Oceanographic Unit were to be short-lived when the unit was closed in April 1982. At that time COIL became the fifth branch of the Port and Environmental Safety Division, Office of Marine Environment and Systems (G-W).

COIL moved to its present location in Groton, Conn., in 1986. In 1988, COIL and the Marine Fire and Safety Research Staff were merged to form the Coast Guard Marine Safety Laboratories. During 1991, control of the Marine Fire and Safety Research program was returned to the Coast Guard R&D Center and COIL became the Marine Safety Laboratory.

Figure 3: Petty Officer 3rd Class Logan Brien, a marine science technician at the USCG Marine Safety Laboratory, prepares oil samples. PA3 Kelly Newlin, USCG.

As part of the Coast Guard's streamlining initiatives in 1996, the laboratory's top leadership position was converted from a Commanding Officer to a Coast Guard civilian supervisory chemist with the title of Manager. MSL is currently a sub-unit of the National Maritime Center (NMC). Planning is presently underway to move MSL under the Coast Guard's Office of Investigations and Analysis (G-MOA).

Overview of Oil Spill Identification Methodology

The Oil Spill Identification System (OIS) uses the unique, intrinsic properties of petroleum oil that make it possible to match spilled oil to the correct chemical source (Figure 3). The system is based on multiple analytical methods. Of the original four techniques developed and evaluated for the OIS, two are still used: gas chromatography (GC) and infrared spectroscopy (IR). Fluorescence spectroscopy (FL) and thin layer chromatography (TLC) are no longer used by MSL. As a result of the development of increasingly sophisticated and powerful analytical instrumentation, gas chromatography-mass spectrometry (GC-MS) has been added as the most powerful analytical technique available for the task.

These analytical methods measure different chemical properties of an oil sample. If two oils are chemically similar, they are said to derive from a common source. In nearly every case, oils from other suspected sources will be simultaneously eliminated from consideration as the pollutant source because they are chemically different, as determined by the test methods.

Interpretation of the analytical test results is not always straightforward because of increased analytical complexity brought about by weathering or contamination of the spilled oil. The term *weathering* includes such actions as: evaporation; dissolution; biodegradation; oxidation; and other chemical, physical, and biological environmental changes that alter the makeup of the spilled oil. The degree of weathering will vary with each particular case, and this can significantly complicate the analyst's job (Figure 4).

MSL prepares a written analysis report for each case. The report is a self-contained document that includes the expert opinion of a trained chemist such as Kristy Juaire, ScM, who has a master's degree in geochemistry from Brown University and has been at MSL for three years. The report consists of a forwarding letter; laboratory report with results and conclusions; sample check-in log; case docu-

Figure 4: Marine Science Technician 1st Class Steven Natale has been at the USCG Marine Safety Laboratory for almost four years. "It takes almost two years to become completely qualified in this lab. However, we are only one of few billets in the Coast Guard that is a science-oriented billet," said Natale. PA3 Kelly Newlin, USCG.

mentation (analysis request, chain-of-custody, etc.); quality assurance sheet; cost-recovery documentation; worksheets and the original test data.

Techniques Used to Analyze Oil

Gas chromatography (GC) separates the components of an oil primarily on the basis of their boiling points. The separation is carried out under controlled conditions such that the same component will be eluted from the gas chromatographic column at the same relative time for all samples. The separated components are sensed by a flame ionization detector and simultaneously recorded electronically. Interpretation of evaporative weathering is relatively straightforward, because it affects components in the same sequence as they are displayed graphically.

Gas chromatography-mass spectrometry (GC-MS) uses a mass selective detector to continuously collect the mass spectrum for the components eluting from the GC. The mass spectrum, reflecting the ion fragments present, can be used to conclusively identify individual components. For oil identification, selected target ions representing biomarkers in the oil are selected. These biomarkers are components unique to petroleum oils; their ratios are used to characterize individual oils. Because some are highly resistant to biodegradation and other weathering, severely weathered oils that cannot be identified by other means can often be matched by GC-MS.

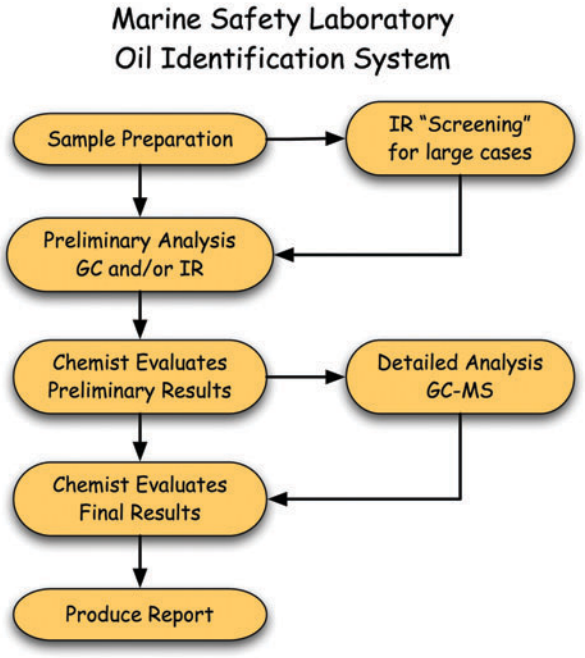


Figure 5: USCG Marine Safety Lab Oil Identification System.

Infrared spectroscopy (IR) uses the absorption of infrared energy over a spectral region that corresponds to the bond stretches and vibrations of the molecules that form the oil. A number of absorptions are common to all petroleum oils. These absorptions allow the analyst to identify the sample as a petroleum product. Other absorptions are used for uniquely identifying specific oil samples. Comparison of the infrared spectra, taking into account weathering differences, is sometimes used to eliminate dissimilar sources from further analysis (Figure 5).

What Do the Results Mean?

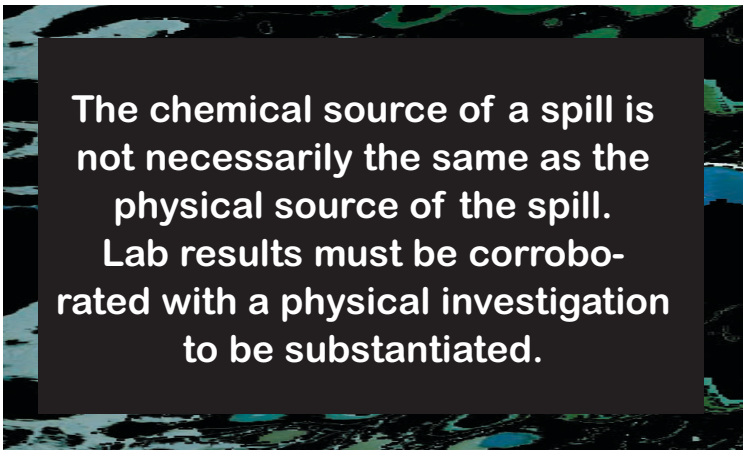
When MSL's report says samples "match," it will specify, for example, that Spill X and Source Y "are derived from a common source." That means they both came from a common chemical source of petroleum oil. Our analytical lab testing cannot prove the physical source of the oil (Figure 6).

Let's use a simplified example of an actual MSL case to demonstrate what this means. The lab receives three samples for analysis: one from the spill (unweathered fuel oil) and two from different suspect sources (both also unweathered fuel oils). The lab reports a "perfect match" between Suspect Source A and the Spill C. Suspect Source B is a clear "non-match" with the Spill C. But, based on his observations at the scene, the field investigator is

convinced that Suspect Source B is the responsible party. In reality, both the lab and the field investigator are correct! How can that be true?

A thorough review of all the paperwork (original sample collection labels, chain of custody, sample preparation documents, etc.) is conducted and does not uncover any errors or inadvertent mix-up of samples. Lab analysis and interpretation of results were repeated with the same conclusion: Source A matches Spill C and Source B does not match.

Armed with this apparent paradoxical result, the field investigator gathered more information. Suspect Source B was found to have had a previously unreported tank rupture that was subsequently repaired and the tank was refilled. Prior to the rupture, both A and B had been filled from the same fuel oil supply. After the leak was repaired, B was refilled from a different fuel oil supply.



Conclusion: The chemical source of a spill is not necessarily the same as the physical source of the spill. Lab results must be corroborated with a physical investigation to be substantiated.

Improving the Overall Process

MSL provides on-call assistance to Coast Guard field investigators, District personnel, Hearing Officers, NPFC, DOJ, and other government agencies on all aspects of the Oil Identification System. This assistance includes but is not limited to:

- Answering questions and explaining the significance of test results.
- Evaluating test data from other laboratories.
- Providing expert witness support.
- Planning sampling strategies in complex cases.

An effective Oil Identification System depends upon good communication and understanding between the various users of the system and Marine Safety Lab personnel. Please give us a call—we're eager to help!

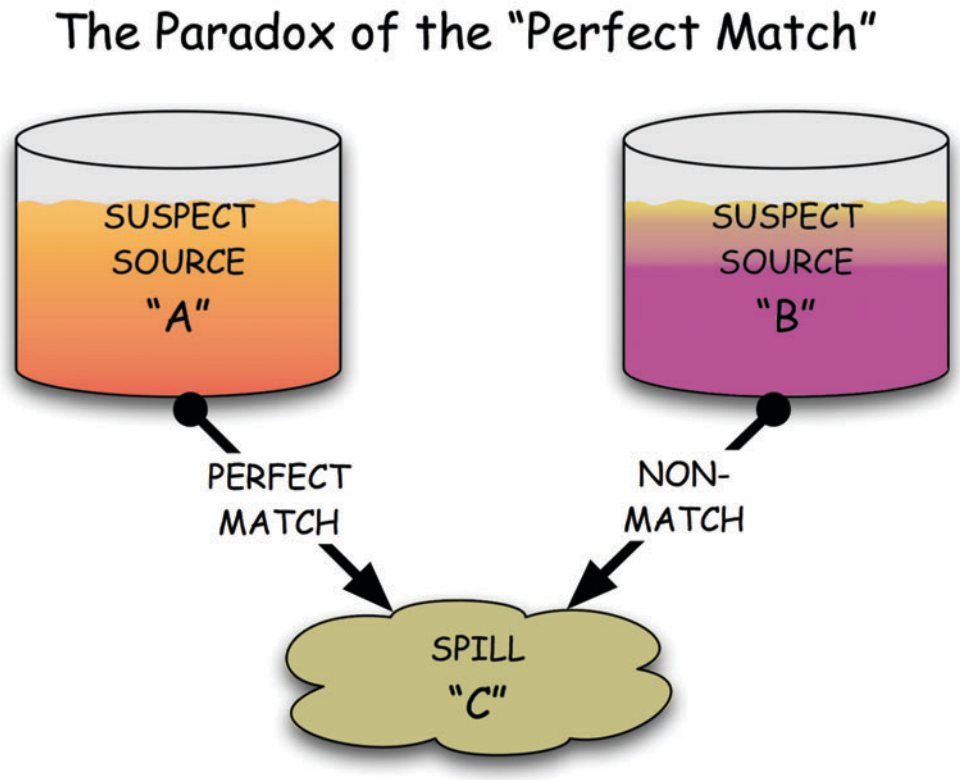


Figure 6: The USCG Marine Safety Laboratory reports a "perfect match" between Suspect Source "A" and the Spill "C" — but, based on his observations at the scene, the field investigator is convinced that Suspect Source "B" is the responsible party. In reality, both the lab and the field investigator are correct!