

DETECTION, IDENTIFICATION, AND QUANTIFICATIONTECHNIQUES FOR SPILLS OF HAZARDOUS CHEMICALS

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## ABSTRACT

In this study, we have evaluated the first 400 chemicals listed in the Coast Guard's Chemical Hazards Response Information System (CHRIS) handbook with respect to their detectability, identifiability, and quantifiability by 12 generalized remote and in situ sensing techniques and some of the pollution sensing instruments that are currently available or which could reasonably be expected to be available within the next few years. We have also attempted to identify some of the key areas in the technology of water pollution sensing in which additional research and development efforts are needed.

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1. INTRODUCTION

The ARGO MERCHANT oil spill and the contamination of the James River by kepone are recent examples of spills of hazardous chemicals into the waterways of the United States. The possibility of water pollution by chemical spills is a continuing problem in our industrial society, and it is likely, with continued growth in petroleum, chemical, and related industries, that the problem will escalate. The Coast Guard and the Environmental Protection Agency (EPA) have been charged by Congress with responsibilities for monitoring pollution in U. S. waterways. Therefore, they require technological capabilities for quickly detecting, identifying and quantifying spills of hazardous chemicals to minimize the impact upon the environment. This study, supported jointly by the Coast Guard and the EPA, was intended to provide some of the initial technical data that is required by those agencies in meeting their responsibilities for pollution monitoring and control.

The problem of detecting, identifying, and quantifying spilled chemicals in large bodies of water such as rivers, lakes, and the oceans is enormously complex. This is due in part to the large number of chemicals that can potentially be spilled, and to the large diversity of the properties exhibited by those chemicals in water. It is also due to environmental factors such as the turbidity, turbulence, and roughness of the water, background pollutant concentration, and atmospheric conditions.

In recent years, rapid and significant advances have been made in the technology of remote sensing. Little more than a decade ago, the state-of-the-art in remote sensing was largely represented by the techniques of aerial photography. Although photographic techniques can be highly effective in certain applications, their range of effectiveness is limited by the relatively narrow spectral range of available films and by the difficulty of quantitatively analyzing photographic imagery. The development of the optical-mechanical scanner was an important step in remote sensing because it provided a means for quantitative data recording via magnetic tape as well as providing a wide-band multispectral capability. More recently, the availability of lasers, photon counters, optical multichannel analyzers and other advanced electro-optical devices have made possible further significant advances in remote sensing capabilities.

Nevertheless, no remote sensing technique or instrumentation system for unattended in situ pollution monitoring is yet available that can adequately detect, identify, or quantify a broad range of chemicals under normal environmental conditions. It is generally recognized that a multisensor approach is required to achieve a reasonably effective operational pollution monitoring

capability. The Coast Guard's AOSS (Airborne Oil Spill Surveillance) system, utilizing radar, passive microwave, thermal infrared, and video (TV) sensors, is an example of a system of this type.

Numerous factors will affect the detectability, identifiability, and quantifiability of a given spilled chemical. The nature and degree of influence of these factors will depend on the type of instrumentation system used. A list of important factors would include:

- type of sensing system - remote or in situ;
- distance from the sensor to the water;
- zenith angle of the observation;
- system sensitivity;
- distance from the source of the spill;
- time since the spill;
- concentration of the chemical;
- turbidity of the water;
- turbulence and surface roughness of the water;
- salinity of the water;
- water depth;
- density of biological organisms;
- background pollutant concentration;
- weather conditions; and
- ambient lighting.

It was not the intent of this study, nor is it feasible, to perform an analysis which takes into account all of these factors. The ways that they individually and in combinations affect remote and in situ sensing measurements could constitute numerous profitable research topics.

In this study, we have evaluated the first 400 chemicals listed in the Coast Guard's Chemical Hazards Response Information System (CHRIS) handbook with respect to their detectability, identifiability, and quantifiability by some of the pollution sensing instruments that are currently available or which could reasonably be expected to be available within the next few years. We have also attempted to identify some of the key areas in the technology of water pollution sensing in which additional research and development efforts are needed.

## 2. METHOD

Our analysis approach utilized generalized sensing system characteristics and the gross physical, chemical, and optical properties of the CHRIS chemicals to sort out the chemicals that are likely to be detectable, identifiable, and quantifiable by each of the twelve sensing methods. This approach yields an estimate of the relative potential detectability, identifiability, and quantifiability of each of the CHRIS chemicals for the twelve sensing techniques. It also yields an estimated, relative, broad-spectrum effectiveness ranking for each of the sensing techniques. Without precisely defining acceptable ranges for environmental conditions, we assumed that a favorable set of environmental conditions exists for each sensing system.

To conduct this study, it was necessary to identify, from a long list of analytical and remote sensing techniques, those techniques which could be both practical and effective in field applications to detect, identify, and quantify chemical spills in water bodies. Appropriate techniques should have several attributes, including the capability of detecting a broad range of chemicals, reliability, stability, capability for unattended or automatic operation, and low power requirements. For in situ sensing systems, an important consideration is that no sample preparation should be required. The following techniques were selected:

1. Optical reflectance;
2. Thermal infrared (passive sensors);
3. Passive microwave;
4. Radar;
5. Fluorescence;
6. Raman scattering;
7. Ion-selective electrodes;
8. Electroconductivity;
9. Reduction-oxidation potential;
10. Optical absorptimetry;
11. Dissolved oxygen;
12. Total oxygen demand.

These systems can be categorized as either "in situ" or "remote" sensing systems. In this study, in situ systems are those which operate in direct contact with the water, and remote systems are those which operate at some distance from the water. Using these definitions, the first six techniques in the above list are primarily applicable to remote sensing. Fluorescence and Raman scattering techniques can also be implemented effectively for in situ applications. The last six techniques are limited to in situ applications.

The ability of a sensor to detect, identify, or quantify a chemical depends largely on the accessibility of the chemical to the sensor. For example, a floating chemical is accessible to a thermal infrared detection system, but a sinking chemical is not. The chemical properties which primarily determine accessibility are:

- Solubility in water;
- Density;
- Vapor pressure;
- Reactivity;

Recognizing that highly volatile or reactive substances constitute a special problem, it was sufficient in this study to focus primarily on the properties of solubility and density. On this basis, each chemical can be assigned to one of four accessibility groups:

| <u>Accessibility<br/>Group</u> | <u>Floats</u> | <u>Soluble</u> |
|--------------------------------|---------------|----------------|
| 1                              | yes           | yes            |
| 2                              | yes           | no             |
| 3                              | no            | yes            |
| 4                              | no            | no             |

Numerical accessibility values were assigned to each accessibility group/sensing system combination. The lower limit on solubility was assumed to be one part per hundred.

The second basic consideration in this analysis is that in order to be detected, identified, or quantified by a given sensing system, a spilled chemical must possess specific optical or electrochemical characteristics. Each chemical was evaluated with respect to those characteristics, and numerical system applicability values were assigned to each chemical/sensing system combination. In many cases, the available data were insufficient. This problem was handled by considering molecular structures, possible ionic strengths, ion mobility, stability under environmental conditions, viscosity, etc. For example, chemical structure is of prime importance in determining the strength of fluorescence.

### 3. RESULTS

The numerical accessibility factors and system applicability factors were combined by digital computer for the 14,400 possible chemical/sensing system/sensing function combinations. The results were displayed in the form of charts or numerical matrices. The numerical analysis yielded:

- 1) The estimated relative, potential effectiveness of each of the 12 generalized sensing techniques for detecting, identifying, and quantifying each of the 400 CHRIS chemicals.
- 2) A numerical estimate of the overall relative, potential detectability, identifiability, and quantifiability of each of the 400 CHRIS chemicals.
- 3) A ranking of the relative effectiveness of each of the 12 generalized sensing techniques for detecting, identifying, and quantifying all 400 CHRIS chemicals.

Because of space limitations these results can only be summarized in a general way here. Figure 1 is a chart which lists the numbers of chemicals from the CHRIS list that are estimated to be potentially detectable, identifiable, and quantifiable by the 12 generalized sensing systems. Also shown in Figure 1 are the corresponding numbers for currently available water pollution sensing instrumentation. These results were derived by using available product information which was not necessarily complete. Nevertheless, these results probably do provide a reasonable estimate of current capabilities. It is vital to realize, however, that in many cases a sensor can only detect, identify, or quantify a given chemical under special circumstances. For example, most of the chemicals listed as detectable by optical reflectance methods are detectable by a specific instrument which is useful but which, nevertheless, has a small field of view and operates at relatively short range.

The analysis indicates that 253 of the 400 CHRIS substances can be detected by at least one available pollution sensor under certain operational and environmental conditions. The identification and quantification capabilities of existing remote and in situ sensing systems appear to be minimal.

### 4. CONCLUSIONS AND RECOMMENDATIONS

It should be stressed that broad-spectrum pollution monitoring is a complicated matter, involving many environmental factors as well as the characteristics and limitations of available instrumentation. It is clear that it is impractical if not impossible to cope with every environmental variation, to put a sensor at every location where pollution is possible, to survey every square mile of water surface or to detect every chemical that is spilled. Studies should, therefore, be made to determine and evaluate the relative probabilities for spillage of each of the CHRIS chemicals, probable spill mechanisms and locations, and areas of probable greatest hazard to the environment and to human health. Theoretical and experimental programs should be initiated and supported to study pollution transport and dispersal mechanisms in crucial areas such as rivers, harbors, and coastal zones. Both generalized and site-specific transport models should be developed for the purpose of predicting the spatial and temporal distributions of chemicals having a wide range of chemical characteristics in water

The optimum design and deployment of pollution sensors as well as effective planning for the control and cleanup of possible chemical spills will require the completion of research programs of this kind.

This study supports the generalization that identification and quantification of chemical spills will be more difficult and costly than the already difficult task of detection alone. Therefore, assuming that funding for the development, deployment, and maintenance of pollution sensing equipment will not be unlimited, it would be useful to consider how much effort should be expended, in the short term, on the development of each of these desired capabilities.

Under certain circumstances, mainly where fixed sensors can be employed, it will not be too difficult to achieve a limited spill identification capability. Several methods are possible. Some, such as Raman scattering and IR reflectance measurements have been included in this study. Others, such as measurements of optical scattering and absorption spectra in the vapor emitted by the chemical, gas chromatography, and multisensor approaches, can be developed. But to develop and implement a comprehensive capability, geared to a wide range of chemicals and operable under a wide range of environmental conditions and spill locations, would require a massive, costly effort. Specific and reasonable needs for identification capabilities should be defined in order to maximize the cost effectiveness of hardware development programs. For the same reasons, the need for quantification capabilities should be similarly considered.

The task of water pollution monitoring requires the surveillance of large areas of oceanic, coastal, and inland waters. For this reason, aerial sensing systems, particularly real-time imaging systems, should receive careful attention and be utilized to the maximum possible extent. Data formats and on-board image display systems should be designed to derive the maximum practicable benefit from the processing power of state-of-the-art digital electronics as well as the pattern recognition sensitivity of the human eye and mind when viewing two-dimensional imagery. The design of data processing, display, and recording instrumentation will be a major factor in determining the effectiveness of aerial remote sensing systems and should not be underemphasized in development programs.

The following items briefly outline several additional suggestions for developing and implementing pollution sensing techniques.

- Raman measurements promise to provide a chemical identification and quantification capability in many in situ and non-aerial remote sensing applications. Efforts should be directed to finding and implementing methods for increasing the signal levels and signal-to-noise ratios of Raman (and fluorescence) measurements. This would include the development of advanced Raman techniques which will allow the separation of a Raman scattering spectrum from a fluorescence spectrum.
- Instrumentation systems which incorporate several kinds of pollution sensors will have much greater capabilities for chemical detection, identification, and quantification than can be obtained from any single sensor. The effectiveness of combining sensors in this way was not explicitly evaluated in this study but it should be evaluated in future work.
- Digital signal processing capabilities are vital for deriving the maximum possible information from remote and in situ sensors. Useful functions include signal averaging, signature recognition, background subtraction, data display, and control of operational modes.
- Several techniques for detecting and identifying molecules of a pollutant in the air have been described in the literature. These techniques have not been included in this study, but should be evaluated in future work.
- A significant group of chemicals are insoluble and heavier than water (Accessibility Group 4). Detection of these chemicals is difficult and unlikely except by placing sensors on the bottom of the water body at the proper locations. The importance of making the effort to detect

these substances, the kinds of sensors to employ, and the definition and location of key monitoring sites should be determined by further studies.

- Interference effects are a problem for in situ sensing methods, particularly in inland and coastal waters. These effects can be caused by ambient chemical or ion concentrations, suspended solids, and natural organic matter. Filtering can reduce the problem somewhat for some in situ sensors. Built-in microprocessors may provide an additional means for reducing the problem in addition to enhancing real-time, automatic, analytical capabilities.
- Optical absorption spectra in the UV-visible spectral region are not available for most of the CHRIS chemicals. These spectra should be measured.
- Thermal IR and microwave emissivity values are not available for most of the CHRIS chemicals. These quantities should be measured in order to implement IR and passive microwave sensing methods effectively.

The potential applicability and effectiveness of twelve generalized remote and in situ sensing techniques have been estimated in this study. But those estimates are only an initial step in what should be a sustained program to evaluate and develop pollution sensing techniques and instrumentation. Field experiments and measurements involving a broad spectrum of chemicals and a wide range of environmental factors are needed together with laboratory measurements that are directly relatable to field measurements. Numerous field and laboratory experiments have been conducted to study the detectability of oil spills, yet the body of knowledge gained from those studies is by no means complete or definitive. The scope of the research needed to deal with a broad range of chemicals will be appreciated if it is realized that oils are among the easiest chemicals to detect.

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| SYSTEM                        | POTENTIAL           |              |              | CURRENT    |              |              |
|-------------------------------|---------------------|--------------|--------------|------------|--------------|--------------|
|                               | DETECTABLE          | IDENTIFIABLE | QUANTIFIABLE | DETECTABLE | IDENTIFIABLE | QUANTIFIABLE |
|                               | OPTICAL REFLECTANCE | 133          | 9            | 0          | 133          | 0            |
| THERMAL INFRARED              | 56                  | 0            | 0            | 56         | 0            | 0            |
| PASSIVE MICROWAVE             | 48                  | 0            | 0            | 40         | 0            | 0            |
| RADAR                         | 79                  | 0            | 0            | 47         | 0            | 0            |
| FLUORESCENCE                  | 40                  | 0            | 36           | 40         | 0            | 36           |
| RAMAN SCATTERING              | 69                  | 69           | 69           | 0          | 0            | 0            |
| ION-SELECTIVE ELECTRODES      | 50                  | 0            | 12           | 50         | 0            | 12           |
| ELECTROCONDUCTIVITY           | 48                  | 0            | 0            | 48         | 0            | 0            |
| REDUCTION-OXIDATION POTENTIAL | 40                  | 0            | 0            | 40         | 0            | 0            |
| OPTICAL ABSORPTIMETRY         | 28                  | 0            | 28           | 28         | 0            | 28           |
| DISSOLVED OXYGEN              | 47                  | 0            | 0            | 47         | 0            | 0            |
| TOTAL OXYGEN DEMAND           | 37                  | 0            | 0            | 37         | 0            | 0            |

FIGURE 1. ANALYSIS SUMMARY. Number of CHRIS chemicals estimated to be potentially and currently detectable, identifiable, and quantifiable by each of the 12 generalized sensing techniques.