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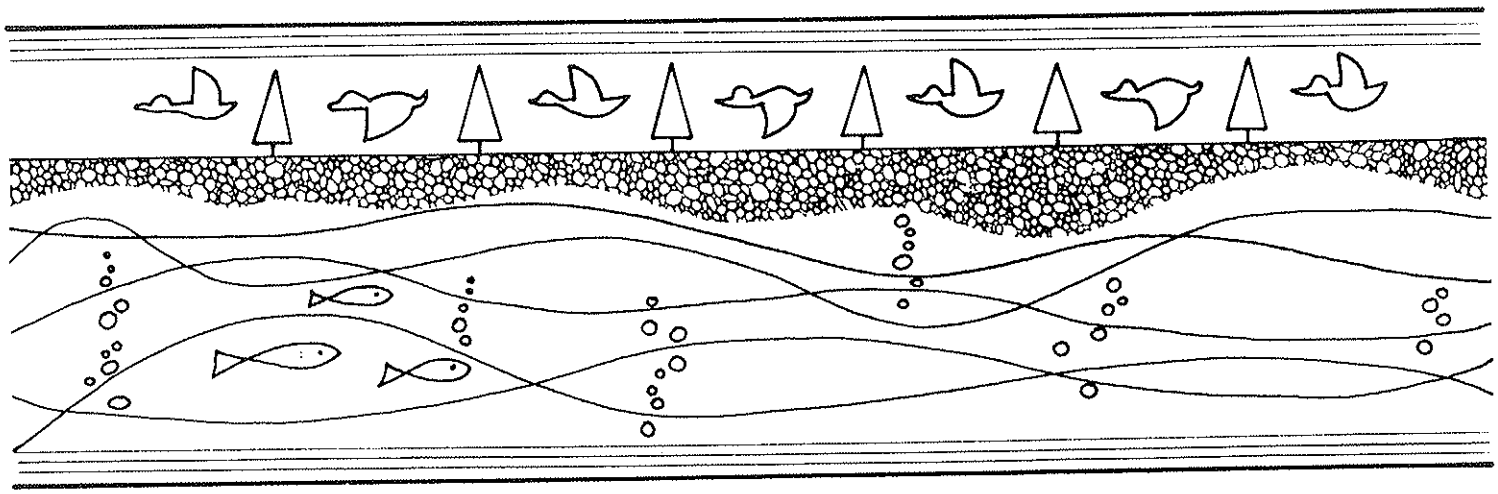

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Disponible en français — voir au verso

Mr. M.F. Fingas and Mr. K.M. Meikle
Technical Editors
Environmental Emergencies Technology Division
Technical Services Branch
Environment Canada - EPS
River Road Labs
Ottawa, Ontario
K1A 1C8

Phone: (613) 998-9622

Mr. Michel Cloutier
Publisher and Coordinator
Technical Services Branch
Environment Canada - EPS
Ottawa, Ontario
K1A 1C8

Phone: (819) 997-3405

The Spill Technology Newsletter was started with modest intentions in 1976 to provide a forum for the exchange of information on oil spill countermeasures and other related matters. We now have over 2000 subscribers in over 40 countries.

To broaden the scope of this newsletter, and to provide more information on industry and foreign activities in the field of oil spill control and prevention, readers are encouraged to submit articles on their work and views in this area.

Disponible en français, s'adresser à la:

Section des publications
Division du transfert technologique et de la formation
Service de la protection de l'environnement
Environnement Canada
Ottawa, Ontario
K1A 1C8

et demandez Bulletin de la lutte contre les déversements

INTRODUCTION

This edition of the Spill Technology Newsletter marks the start of the eleventh year of publication. It also implements the decision to change it to a quarterly publication. We hope that the reduction in frequency will enable us to stay on schedule in the future.

All three articles in this issue are by members of the staff of EETD. The first is by Alice Bobra and is a summary of the division's program to develop improved spill analytical systems for use in the field. The second is by Harry Whittaker, who reviews membrane technology as it applies to the Oil Industry. The third is by Merv Fingas, who presents results of oil dispersibility determinations. Good reading!

REPORTS AND PUBLICATIONS

- CONCAWE (the Oil Industry's European organization for environmental and health protection) has released the following two reports; "Strategies for the assessment of the biological impacts of large coastal oil spills - European coasts" Report No. 5/85 and "Trends in Oil Discharge with Aqueous Effluents from Oil Refineries in Western Europe - 1984 Survey." Report No. 8/85. These reports are available from CONCAWE, Babylon - Kantoren A, Koningin Julianaplein 30-9, 2595 AA, den Haag, Netherlands, phone 31 70 47 5494.

- The Environmental Protection Service has now released thirty-one EnviroTIPS publications. These provide comprehensive spill-related data related to properties, behaviour and environmental and safety aspects of a chemical. Each publication is about 100 pages and is intended for a technically-oriented audience. EnviroTIPS may be obtained from: Publications Coordinator, Technology Development and Technical Services Branch, Environmental Protection Service, Ottawa, Ontario, K1A 1C8. The following manuals are available:

Acetic Anhydride
Ammonia
Ammonium Nitrate
Ammonium Phosphates
Benzene
Calcium Chloride
Calcium Oxide
Carbon Dioxide
Chlorine
2-Ethylhexanol
Ethylbenzene
Ethylene
Ethylene Dichloride
Ethylene Glycol
Ferric Chloride
Hydrogen Chloride/Hydrochloric Acid
Hydrogen Fluoride/Hydrofluoric Acid
Hydrogen Sulphide
Mercury
Morpholine
Natural Gas
Phosphorus
Propylene
Sodium Hypochlorite
Sodium Chloride
Sodium Hydroxide
Styrene
Sulphur
Sulphuric Acid
Toluene
Xylenes

- The "World Catalog of Oil Spill Response Products", edited by Robert Schulze is available from "World Catalog", 6154 Rockburn Hill Rd., Elkridge, Maryland, 21227,

phone (301) 796-0551. The price is $50 (U.S.) in the U.S.A. and $60 (U.S.) for Canada and overseas. Handling and shipping charges are $4 per copy, shipping in the U.S. $1 and $3 elsewhere, and by air $8. The book is a catalogue of equipment - mostly booms and skimmers plus a description of their use and limitations. The report has also drawn on information contained in "a catalogue of skimmers" published by EPS, and the draft of EPS's soon to be published, "Catalogue of Booms".

- The Environmental Emergencies Technology Division has released twenty-one script reports, the titles of which appear below. For copies of these reports contact: Publications Coordinator, Technology Development and Environmental Protection Service, Ottawa, Ontario, K1A 1C8.

"A Review of the Fate and Behaviour of Oil in Cold Climates" (EE-74)

"Oil Spill Countermeasures for Low-energy Shorelines in Canada - Research Recommendations" (EE-73)

"Multi Hit Dispersion of Oil Spills" (EE-72)

"An Overview of the Biodegradation of Chlorinated Hydrocarbons" (EE-71)

"A Study of Frequently Spilled Mixtures" (EE-70)

"Continuing Development of the Person-portable Analytical System" (EE-69)

"Evaluation of Remote Sensing Technology for Monitoring Chronic Oil Discharges from Offshore Well Sites" (EE-68)

"Data Management and Estimation of Physical and Chemical Properties of Spilled Chemicals" (EE-67)

"Determination of Oceanographic Factors Associated with the Subsurface Movement of Oil" (EE-66)

"Oil Spill Remote Sensing Equipment Test Protocol" (EE-65)

"A Model of the Long-term Fate of Chemical Spills" (EE-64)

"The AMOCO CADIZ Incident - Site Visits Seven Years After the Spill" (EE-63)

"Statistical Description of Pack Ice in the Beaufort Sea, Lancaster Sound and the Labrador Sea" (EE-62)

"A Study of Pipeline Leak Detection Technology" (EE-61)

"In-situ Burning of Uncontained Oil Slicks" (EE-60)

"The Evaporation of Volatile Liquids" (EE-59)

"Report on the Beaufort Sea Small Scale Oil Spill Dispersant Trial" (EE-58)

"A Catalogue of Crude Oil and Oil Product Properties" (EE-57)

"Igniter Requirements for a Major Oil Spill From a Vessel in the Canadian Arctic" (EE-56)

"A Design for an Experiment to Monitor the Physical Fate of Oil Spilled in an Open Ocean Environment" (EE-55)

"Remote Sensing Equipment for Chronic Oil Discharges" (EE-54)

Seven working reports on the Baffin Island Oil Spill Project have recently been released. Copies of the reports may be obtained from: Publications Section, Environmental Protection Service, Ottawa, Ontario, K1A 1C8, phone (819) 997-3405. The citations for these reports are as follows:

Humphrey, B. 1984. Chemistry 1: Field Sampling and Measurements - 1983 Study Results. Baffin Island Oil Spill Working Report 83-1; 64 p. Environmental Protection Service, Environment Canada, Ottawa.

Boehm, P., W. Steinhauer, D. Cobb, S. Duffy and J. Brown. 1984. Chemistry 2: Analytical Biogeochemistry - 1983 Study Results. Baffin Island Oil Spill Working Report 83-2; 139 p. Environmental Protection Service, Environment Canada, Ottawa.

Cross, W.E., D.H. Thomson, C.M. Martin, M.F. Fabijan. 1984. Macrobenthos - 1983 Study Results. Baffin Island Oil Spill Working Report 83-3; 176 p. Environmental Protection Service. Environment Canada, Ottawa.

Owens, H. 1984. Shoreline Countermeasures - 1983 Results. Baffin Island Oil Spill Project Working Report 83-4. Environmental Protection Service, Environment Canada, Ottawa.

Bunch, J.N. and T. Cartier. 1984. Microbiology: 1. Effects of Petroleum Releases on the Microheterotrophic Flora of Arctic Sediments -- Effects After Two Years. Baffin Island Oil Spill (BIOS) Project Working Report 83-5: x + 44 p. Environmental Protection Service, Environment Canada, Ottawa, Ontario.

Eimhjellen, K. and K. Josefsen. 1984. Microbiology 2: Biodegradation of Stranded Oil - 1983 Results. Baffin Island Oil Spill Project Working Report 83-6: 58 p. Environmental Protection Service, Environment Canada, Ottawa.

Mageau, C. and R. Engelhardt. 1984. Behavioural and Physiological Effects of Hydrocarbon Exposure on Selected Arctic Invertebrates. Baffin Island Oil Spill Working Report 83-7: Toxicology. Environmental Protection Service, Environment Canada, Ottawa.

Gilfillan, E. and D. Vallas. 1984. Observations of Scope for Growth, Aspartate Aminotransferase Activity and Glucose-6-Phosphate Dehydrogenase Activity in Mya Truncata and Serripes Groenlandicus Exposed to Various Concentrations of Chemically Dispersed Crude Oil. Baffin Island Oil Spill Working Report 83-7: Toxicology. Environmental Protection Service, Environment Canada, Ottawa.

UPCOMING CONFERENCES

- The Ninth Annual Arctic and Marine Oilspill Technical Seminar will be held June 10-12, 1986 at the Chateau Lacombe Hotel in Edmonton, Alberta. Registration fees will be $90. For further information contact; Seminar Coordinator at (819) 997-3405.
- The Thirteenth Annual Aquatic Toxicity Workshop will be held in Moncton, New Brunswick from November 11 to 14, 1986. For further information contact: Prof. J.S.S. Lakshminarayana, Department of Biology, University of Moncton, Moncton, New Brunswick, E1A 3E9, phone (506) 858-4323.
- "Emergency Response - 86", an International Symposium Focussing on Transportation Emergency Response Systems for Dangerous Goods will be held in Vancouver, British Columbia, September 14-18, 1986. The Symposium is planned in conjunction with EXPO 86, the world exposition on transportation and communications. For further information contact; Mrs. Laurie Hogan, Canadian Chemical Producers' Association, Suite 805, 350 Sparks Street, Ottawa, Ontario, K1R 7S8, phone (613) 237-6215.
- The Fourth Annual Technical Seminar on Chemical Spills will be held at the Sheraton Centre, Toronto, Ontario, February 10-12, 1987. For information on technical papers call Merv Fingas at (613) 998-9622. For other information on the seminar contact; Seminar Coordinator at (819) 997-3405.

BRIEF NOTES

- Dr. Patrick McLaren has left the Geological Survey of Canada and has formed GeoSea Consulting, specializing in the use of sediment transport patterns to predict, amongst other things, the fate of oil on the sea bottom and the dispersal of toxic waste. His temporary address is:

  Department of Earth Sciences
  University of Cambridge
  Downing Street
  Cambridge, England
  CB2 3EQ

  Phone: (0223) 355463 ext. 223

  or (0223) 316257

Can-Ross industries in Oakville is marketing a polypropylene sorbent, "Matasorb". For further information contact Ted Edgar, Can-Ross Environmental Services Ltd., 1476 Speers Road, Oakville, Ontario, L6L 2X6, phone (416) 825-3638.

ENVIRONMENT CANADA'S PROJECT FOR VEHICLE AND PERSONAL PORTABLE ANALYTICAL SYSTEMS FOR CHEMICAL EMERGENCIES

Submitted by: A.M. Bobra
Environmental Emergencies Technology Division
Environmental Protection Service
Ottawa, Ontario

Introduction

Following a major chemical spill, effective response measures are needed for the preservation of human life and health, the minimization of property damage, the protection of the natural environment and the utilization of collection systems and chemical/physical treatment systems. In order to choose the most appropriate of these response measures for the specific spill incident it is necessary for the responders to have a knowledge of the physical/chemical properties, and human and environmental toxicity data of the substances involved. In addition, it is imperative to have analytical systems which are capable of rapid, on-site determinations of what has been spilled and of its concentration in air, water and soil (Fingas, 1984; Fingas, 1982).

Recognizing that these analytical requirements were not adequately met in most spill situations, the Environmental Emergencies Technology Division (EETD) of Environment Canada began a program in 1980 to develop analytical methods suitable for spill response. This program is part of the Chemical Hazards Emergency Countermeasures (CHEC) program. Existing methods and instrumentation were reviewed and grouped into five classifications, or levels, based on criteria of portability, accuracy and complexity. The levels are as follows; Level 1 - pocket-portable equipment based on reagent colour changes, Level 2 - person-portable detectors based on electronic meter detectors, Level 3 - vehicle-portable instruments normally found in a fixed laboratory combined with microcomputer technology to simplify operation, Level 4 - mobile laboratory (towable on good roads) and Level 5 - fixed laboratory (non-portable). Levels 1, 2 and 3 were considered most appropriate for spill monitoring and EETD decided to actively pursue methods according to these levels. In each case the equipment is to be suitable for use by personnel without extensive training in chemistry or analytical instrumentation methodology and working under emergency conditions. Development work on each of the three levels is warranted since they each have unique advantages. For example, Level 2 instrumentation is more easily transportable than Level 3 instrumentation and will most likely require less maintenance and operator training. This

will permit analysis to be done directly at a remote site. However, in most cases, it will not be as accurate or as sensitive as Level 3 and the identity of the spilled substance must be known.

To focus the development of these analytical capabilities, a priority list of 150 chemicals was developed by EETD in 1982 (Fingas, 1982) based on spill frequency and spill consequences. The chemicals on the list accounted for over 90 percent of known chemical spills and spill volume in Canada. EETD research on the various levels of analytical capability was geared to the chemicals on the list.

Person-Portable Analytical System (Level 2)

Initial work on the Level 2 system involved evaluating a wide range of commercially available instruments and methods. Accuracy, ease of use, and the capability to analyse a large number of the chemicals on EETD's priority substances list were considered as important criteria for choosing equipment to adapt to the spill site monitoring program. Air monitoring instruments which satisfied these criteria were the Foxboro Model 128 Organic Vapour Analyser (OVA) and the HNU System Inc. PI-101 Photoionization Analyser (HNU). Accordingly, work to date has focussed on the OVA and HNU for air analysis.

The OVA 128 is basically a portable flame ionization detector (FID). In operation, a continuous metered flow of sample air is drawn into the detector chamber where organic molecules are burned in a hydrogen flame, producing positively-charged carbon-containing ions. These ions are driven to a negatively-charged collector electrode where a current is generated which is proportional to the ion collection rate. This current is measured with a pre-amplifier, the output signal from which is further amplified and displayed on the meter assembly situated on the hand-held probe assembly. The detector exhibits inherently high sensitivity and responds to a wide range of organic chemicals. The OVA has its own hydrogen supply and a rechargeable 12V DC battery allowing for a minimum of eight hours of continuous operation.

The HNU PI-101 is basically a portable photoionization detector (PID). In operation, a continuous flow of sample air is drawn by a DC-powered fan into an ionization chamber located on a hand-held probe. Photons emitted by the 10.2 eV UV source pass through a transmitting window into the ionization chamber where this radiation is absorbed by molecules having ionization potentials of approximately 10.2 eV or less. The positive ions produced are driven to a collector electrode, where a current proportional to the concentration of the sample substance in air is generated. This

current is amplified and used to drive a meter on the readout unit. The HNU is a selective detector since chemicals having ionization potentials much higher than 10.2 eV will not be ionized and therefore will not produce an instrument response. The HNU is capable of detecting a broad range of organic compounds, and can also detect a few inorganic compounds (e.g. H_2 and NO_2). Similar to the OVA, the HNU utilizes a rechargeable battery which allows for 10 hours of continuous service.

Both these instruments are non-specific with respect to measuring a certain chemical out of a mixture of several chemicals. In combination these detectors can be used to detect a great variety of substances. They determine total vapours present at a spill site according to the response of the specific detector used. This is not a drawback, for in most spill situations only one substance is involved and it is easily identified by shipping labels or waybills; moreover, the concentration of that substance is usually far greater than that of the ambient background.

Recent efforts have been directed towards bringing the OVA and HNU work to the "field-ready" stage (Townshend-Colford, 1986; Underdown and Townshend-Colford, 1984; Townshend-Colford and Underdown, 1985; Halman et al, 1984; Lockwood and Halman, 1983). The following tasks have been completed:

1) Calibration experiments for most of the gases and vapours from the EETD priority list chemicals on the OVA and HNU instruments. Response calibration data for a total of 49 substances on the OVA and 39 substances on the HNU were obtained. The vast majority of these are pure compounds although a few are mixtures which are produced for commercial use. Table 1 lists all priority list substances for which data were obtained.
2) Several studies on factors which affect the accuracy of readings from these instruments and which are relevant to spill site conditions.
3) Conversion of the OVA and HNU calibration data to a form usable by spill responders (i.e. scale overlays and primary calibration procedures.)
4) Development of field manuals for the OVA and HNU instruments. These manuals will be used with the meter scale overlays and associated primary calibration procedures.
5) Development of a training program for spill responders who will be using the Level 2 personal-portable analytical system.

For water and soil analysis of organic and inorganic substances, the Hach Company Direct Reading Engineer's Laboratory Model DR-EL/4 (Hach Kit) was chosen as

the most suitable available unit that could be modified to satisfy the Level 2 criteria. The Hach Kit is a portable laboratory containing a spectrophotometer/conductivity meter, digital titrator, pH meter, basic glassware and pre-packaged reagents. Included with the Kit is a well-written, easily understood manual which provides detailed step-by-step procedures. This enables the Hach Kit to be used by personnel who have not received extensive training in laboratory analysis or instrumentation. The Hach Kit has been widely used for water quality analysis in laboratories and water treatment plants. With the exception of phenol, all the methods are geared to analysing inorganic substances in water.

All of the inorganic substances from the priority list, except for hydrogen peroxide and titanium dioxide, can be detected in water using the existing methodology of the Hach Kit. The first step in the modification of the Hach Kit was to develop methods for analysing inorganic substances in soil. It has been determined that the methods used for analysis of inorganic substances in water can be easily modified for soil samples by simply extracting the soil sample with water first and then proceeding with the method. The next step in the modification of the Hach Kit was to find suitable methods for the analysis of organic substances from the priority list. Initially, the 150 priority list chemicals were arranged into groups, each of which could be amenable to analysis by a single method. Following this grouping, a literature search was undertaken than included published methods for quantitative analysis of water, qualitative or "spot tests" which normally are used to detect the presence or absence of a chemical, and physical-chemical properties. The most sought-after methods were those that would involve adding pre-measured, packaged reagent to samples (aqueous or soil extracts), allowing a coloured product to develop, and measuring the colour intensity with a colourimeter. Methods using the digital titrator were also sought. Specific, known amounts of reagents can be added to the sample to produce a colour or a change in colour. Using the titrimetric method, the same colour is produced, but the varying amounts of titrant added correspond to a range of concentrations of the sample.

Following the literature review, a preliminary evaluation of the methodologies was done to see if these analyses could theoretically be performed successfully in the field using the Level 2 criteria. Those methods that passed the preliminary evaluation were evaluated experimentally. This evaluation addressed the aspects of stability, interferences, sensitivity and detection limits in deionized water and in a loamy soil (Townshend-Colford, 1986).

The work currently in progress and that planned for the future consists of the following:

1) developing methods for the collection of water and soil samples in the field,
2) continuing experimental evaluations of methods which have met the Level 2 criteria,
3) testing the methods with various types of soils,
4) performing calibration experiments for the EETD priority list chemicals,
5) converting the calibration data to a form usable by spill responders (i.e. meter scale overlays for the colourimeter and a table or graph for the titrator),
6) expanding the Hach Kit Manual to include the tests for organics developed in this study which comply with the Level 2 criteria, and
7) developing a training course for spill responders on how to use the modified Hach Kit.

Table 1 also presents a summary of the present and proposed capabilities for measuring spilled substances in air, water and soil.

Vehicle-Portable Analytical System (Level 3)

This system is intended to provide field analysis from a vehicle, which will result in a significant time-saving over transport to a fixed laboratory. It will have a greater inherent accuracy than the pocket and personal portable systems, and will also have the capability to handle samples containing more than one detectable substance. It is anticipated that the vehicle-portable analytical system capability would be needed at spills of highly toxic substances, at spills of more than one substance, and in situations where samples of complex media (e.g. soils) are involved. The Level 3 concept involves equipment which would normally be found in a fixed laboratory and operated by a trained operator. The equipment would be installed in a small van that would also have some support equipment, electrical power, a suitable climate for operation, protective equipment for the operator and the Levels 1 and 2 systems. The equipment would make use of available microprocessor technology and the associated software to make it possible for a person without extensive training in chemistry or analytical techniques, and working under emergency conditions, to operate the instrument and obtain results useful for spill response. This is accomplished by providing a user-friendly interface during the data acquisition and analysis steps, and by performing certain control and analysis tasks normally done by an operator with extensive chemical training.

After having developed these concepts, Environment Canada proceeded to assess the potential application of commercially available analytical instrumentation. A Perkin-Elmer Sigma 2000 Gas Chromatograph (GC) was selected by EETD for initial development as a vehicle-portable analytical system (Bobra, 1986; Bobra 1985; Lockwood and Halman, 1983). The GC was equipped with a photoionization detector (PID), a flame ionization detector (FID) and a electron capture detector (ECD). The gas chromatograph was also equipped with a 2 meter 3% SP-2100/100-120 Supelcoport packed column, a 30 meter DB-5 Megabore column and both standard flash evaporation and head-space sampling options. The gas chromatograph oven was temperature programmed from 50°C to 220°C at a rate of 10°/min. The FID is a universal detector for organic compounds and the PID is more selective for organic compounds and can also respond to several inorganic compounds. Since the PID is essentially a non-destructive detector, the effluent from this detector is directed to the FID, without splitting the stream across two detectors. The PID and FID detectors complement the person-portable air monitoring detector systems currently being used by Environment Canada (i.e. HNU and OVA) and should be suitable for most field applications. Also, an ECD has been added to the GC for the analysis of polychlorinated biphenyls. This detector can be switched on when the sample is expected to contain PCB's or other halogenated compounds to which the ECD responds. The head-space sampler can be used for direct analysis of organic priority chemicals in water, soil and sorbents, eliminating the need for extensive sampling preparation (e.g. extraction, clean-up, concentrating).

The GC has been interfaced to a IBM PC/XT micro-computer with Labnet Communication System and Spectra Physics 4270 Computing Integrator, which is capable of real-time data acquisition and post run data manipulation. The computer can handle data from two detectors simultaneously.

Currently, the existing software is being further modified and developed for user-friendly control of data acquisition, storage and preliminary processing. Preliminary processing consists of searching the data for peaks, computing their areas, retention times and relative retention times when compared to a standard, calculating concentrations present by knowing instrument response factors and calibration studies for each substance, and finally reporting this information. Software is also being developed for a library-based system to make the analysis and identification of samples possible under the vehicle-portable analytical system conditions. This will involve producing a library of retention times for specific pure compounds and for specific mixtures (e.g. fingerprinting of Aroclors or crude oils) and storing calibration results and response factors for

substances on the priority chemical list. In order to correct the effects of instrumentation and column factors, the data will be stored as values relative to a standard sample run on the same day. The operator at a spill site will also have to run a standard as well as the field samples. The software will then compare the field value to those in the library and report compounds of the closest fits for identification purposes (the most probable substances) and amounts present. In addition to the retention time, an identification criterion will be the relative response of the PID, FID and ECD to a given substance (individually or in a mixture) and the relative responses from two of the previously mentioned columns. This system will be able to identify compounds in the following situations:

- when only one pure compound is spilled (e.g. hexane);
- when a mixture of several pure compounds is spilled (e.g. hexane, benzene, toluene and methanol);
- when a mixture of many compounds (e.g. crude oils and PCBs which upon analysis by GC give a characteristic trace) is spilled;
- when a pure compound is spilled with a mixture of many compounds (e.g. methanol and PCBs); and
- when two mixtures of many compounds are spilled (e.g. crude oil with PCBs).

These modifications and development for user-friendly control of data acquisition, storage and preliminary processing and for a library-based system to make the analysis and identification of samples possible under the vehicle-portable analytical system conditions will be completed soon.

Calibrations for 50 compounds from the priority list will be completed for all three media in the near future. These compounds are listed in Table 2. It is believed that this system can be programmed for several hundred compounds.

Currently, the system is being installed into a 1986 compact Ford cargo van. The van has a load capacity of 4000 lb. and the dimensions of the cargo space are 80" (height) x 80" (width) x 148" (length). An air conditioner, generator, line regulator, propane heater and fan are mounted in the van. An air filtration and pressurization system and sampling devices are also included. Vibration/shock mounts are provided for all instrumentation. Benches, cabinets and cupboards are being installed.

The vehicle-portable analytical system will be field tested following completion of the installation and calibration for 50 compounds in all three media. We hope to do this later this year.

The Future of Spill Analytical Systems

The developments to date have shown that vehicle-portable and person-portable analytical systems are possible for spill incidents. New technology will provide capability to monitor more compounds and also to decrease the size and weight of the system. With the concurrent decrease in price, response organizations can be equipped in future years for quantitatively and qualitatively monitoring highly toxic substances. This will allow spill responders to choose the most appropriate cautionary and corrective response measures for that specific spill incident.

References

Bobra, A. (1986). "Continuing Development of a Vehicle-Portable Analytical System", Proceedings of 1986 Technical Seminar on Chemical Spills, Feb. 5-7, Montreal, Quebec.

Bobra, A. (1985). "Development of a Vehicle-Portable Analytical System for Chemical Emergencies", Proceedings of 1985 Technical Seminar on Chemical Spills, Feb. 5-7, Toronto, Ontario.

Fingas, M.F. (1984). "The Development of Improved Countermeasures for Chemical Spills in Canada", Proceedings of 1984 Hazardous Material Spill Conference, April 9-15, Nashville, Tennessee.

Fingas, M.F. (1982). "The Hazardous Material Spill Program of the Environmental Emergency Branch", Spill Technology Newsletter, Vo. 7(2), EPS, Ottawa, Ontario.

Halman, R., Lockwood, J. and Farrington, M. (1984). "Development of a Person-portable Analytical System for Environmental Emergencies", EE-52, EPS, Ottawa, Ontario.

Lockwood, J. and Halman, R. (1983). "Person-portable Systems for Multi-media Analysis", Proceedings of 1983 Technical Seminar on Chemical Spills, Oct. 25-27, Toronto, Ontario.

Lockwood, J. and Halman, R. (1983). "Vehicle-portable Systems for Multi-media Analysis at Chemical Spill Sites", Proceedings of 1983 Technical Seminar on Chemical Spills, Oct. 25-27, Toronto, Ontario.

Townshend-Colford, M. (1986). "Continuing Development of a Person-portable Analytical System", Proceedings of 1986 Technical Seminar on Chemical Spills, Feb. 5-7, Montreal, Quebec.

Townshend-Colford, M. and Underdown, A.W. (1985). "Continuing Development of the Person-portable Analytical System", EE-69, EPS, Ottawa, Ontario.

Underdown, A. and Townshend-Colford, M. (1985). "Development of a Person-portable Analytical System", Proceedings of the 1985 Technical Seminar on Chemical Spills, Feb. 5-7, Toronto, Ontario.

TABLE 1 ANALYTICAL CAPABILITY FOR THE LEVEL 2 SYSTEM

AIR

Priority Materials Covered to Date

Acetic Acid
Acetic Anhydride
Acetone
Acetylene
Acrylonitrile
Ammonia
Benzene
Butadiene
Butanol
Butylene
Butyraldehydes
Carbon Disulfide
Carbon Tetrachloride
Chloroform
Fresh Crude Oil
Cyclohexane
Dichlorobenzene
Dichloroethane
Dimethyl Ether
Ethanol
Ethylbenzene
Ethylene
Ethylene Dibromide
Ethylene Oxide
Ethyl Hexanol
Fluorochloromethanes
Formaldehyde
Gasoline
Heptane
n-Hexane
Hydrogen Sulfide
Isopropanol
Methane
Methanol
Methylamines
Methylene Chloride
Methyl Ethyl Ketone
Methyl Isobutyl Ketone
Methyl Methacrylate
Morpholine
Propylene
Propylene Glycol
Propylene Oxide
Styrene
Toluene
Turpentine
Vinyl Acetate
Vinyl Chloride
Xylenes

Potential Chemicals in Near Future

None

WATER

Priority Material Covered to Date

Acetic Acid
Adipic Acid
Aluminum Chloride
Aluminum Hydroxide
Aluminum Sulfate
Ammonia
Ammonium Chloride
Ammonium Nitrate
Ammonium Phosphates
Ammonium Sulfate
Hydrogen Fluoride/Acid
Lead Chromate
Lead Oxide
Magnesium Hydroxide
Nitric Acid
Nitrilotriacetic Acid
Phenols
Phosphoric Acid
Potash
Potassium Hydroxide

TABLE 1 ANALYTICAL CAPABILITY FOR THE LEVEL 2 SYSTEM (Cont'd)

Barium Sulfate
Benzoic Acid
Boric Acid
Calcium Carbonate
Calcium Chloride
Calcium Hydroxide
Calcium Hypochlorite
Calcium Oxide
Calcium Phosphate
Chlorine
Copper Sulphate
Ferric Chloride
Formic Acid
Hydrogen Chloride/Acid
Potassium Sulfate
Sodium Arsenite
Sodium Chlorate
Sodium Chloride
Sodium Cyanide
Sodium Hydroxide
Sodium Phosphate
Sodium Silicates
Sodium Sulfate
Sulphuric Acid (and Oleum)
Sulfuryl Chloride
Zinc Chloride
Zinc Oxide
Zinc Sulphate

Potential Chemicals in the Near Future

Acetic Anhydride
Acetone
Acrylonitrile
Benzene
Butyraldehydes
Carbon Tetrachloride
Chloroform
Cresol
Cumene
Ethanolamine
Ethylbenzene
Ethylene Dibromide
Ethylene Glycol
Formaldehyde
Hydrogen Peroxide
Maleic Anhydride
Methanol
Methyl Ethyl Ketone
Methyl Isobutyl Ketone
Morpholine
Nonylphenol
PCBs
Phenols
Phthalic Anhydride
Propylene Glycol
Styrene
p-Terphenyl
Toluene
Urea
Vinyl Acetate
Xylenes

SOIL

Priority Material Covered to Date

None

Potential Chemicals in Near Future

Acetic Acid
Acetone
Adipic Acid
Aluminum Chloride
Lead Oxides
Magnesium Hydroxide
Maleic Anhydride
Methanol

TABLE 1 ANALYTICAL CAPABILITY FOR THE LEVEL 2 SYSTEM (Cont'd)

Aluminum Hydroxide	Methyl Ethyl Ketone
Aluminum Sulfate	Methyl Isobutyl Ketone
Ammonia	Nitric Acid
Ammonium Chloride	Nitrilotriacetic Acid
Ammonium Nitrate	Nonylphenol
Ammonium Phosphates	PCBs
Ammonium Sulphate	Phenols
Barium Sulphate	Phosphoric Acid
Benzene	Potash
Benzoic Acid	Potassium Hydroxide
Boric Acid	Potassium Sulphate
Butyraldehydes	Propylene Glycol
Calcium Carbonate	Sodium Arsenite
Calcium Chloride	Sodium Chlorate
Calcium Hydroxide	Sodium Chloride
Calcium Hypochlorite	Sodium Cyanide
Calcium Oxide	Sodium Hydroxide
Calcium Phosphate	Sodium Phosphate
Chlorine	Sodium Silicates
Copper Sulphate	Sodium Sulfate
Cresol	Styrene
Cumene	Sulphuric Acid (and Oleum)
Ethanolamine	Sulfuryl Chloride
Ethylbenzene	p-Terphenyl
Ethylene Glycol	Toluene
Ferric Chloride	Urea
Formaldehyde	Vinyl Acetate
Formic Acid	Xylenes
Hydrogen Chloride/Acid	Zinc Chloride
Hydrogen Fluoride/Acid	Zinc Oxide
Lead Chromate	Zinc Sulfate

TABLE 2 POTENTIAL CHEMICALS IN THE NEAR FUTURE FOR THE LEVEL 3 SYSTEM IN AIR, WATER AND SOIL

Acetic Anhydride	Isopropanol
Acetone	Isopropylbenzene
Acetylene	Malathion
Aminocarb Pesticide (Matacil)	Methanol
Ammonia	Methyl Ethyl Ketone
Benzene	Methyl Isobutyl Ketone
Butanols	Methylene Chloride
Butylene	Naphtha
Butyraldehydes	Natural Gas
Carbon Disulfide	Nonyl Phenol
Chloroform	Pentachlorophenols
Cyclohexane	Perchloroethylene
Dichlorobenzene	Polychlorinated Biphenyls
Ethanol	Propylene
Ethylbenzene	Styrene
Ethylene	Terphenyls
Crude Oil	Toluene
Ethylene Dibromide	Triallate Pesticide
Ethylene Dichloride	Trichlorfon Pesticide
Ethylene Glycol	Trifluralin Pesticide
2-Ethylhexanol	Trinitrotoluene
Fluorochloromethane	Turpentine
Formaldehyde	Vinyl Acetate
n-Hexane	Vinyl Chloride
Hydrogen Sulfide	Xylenes

MEMBRANE TECHNOLOGY IN THE OIL PATCH

Submitted by: Harry Whittaker
Environmental Emergencies Technology Division
Environmental Protection Service
Ottawa, Ontario

Membrane Technology

Membrane technology encompasses the various types of separation techniques which employ a semipermeable membrane. Among those commonly employed are:

Microfiltration (MF)
Ultrafiltration (UF)
Reverse Osmosis (RO)
Gas Separation (GS)
Electrodialysis (ED).

The first three of these constitute a somewhat artificial breakout of what is in fact a gradient of capabilities of solute/solvent separation based on solute particle size. A traditional breakout is shown in Figure 1 where there is a 10^2 difference in particle size between divisions. The artificial nature of this breakout is clearly shown in Figure 2. In the past few years, the overlap among MF, UF and RO has increased further.

Although there is an overlap in the particle (solute) size rejection among MF, UF and RO, there is a definite difference in the explanations for the phenomena. MF and UF, particularly the former, are filtration processes with the particle or molecule rejected based almost completely on size. RO is not, however, in the same category. The size of the "holes" in the membrane is often far smaller than those of the molecules or molecular clusters which pass through. The mechanism in this case is one of solution-diffusion. The molecule (or cluster) dissolves in the membrane material, diffuses through and then is desorbed on the other side of the active membrane. The veracity of this explanation is shown in the case of sodium chloride and phenol interaction with a cellulose acetate membrane. The phenol molecule is larger than sodium chloride yet the latter is rejected while the former is not (1).

Gas separation and electrodialysis are, in fact, applications of RO technology to different conditions. GS is simply gaseous phase RO while ED is RO in the presence of an electric field.

Membrane Technology Applications

The areas of use of membrane technology have become very wide spread in the past few years. This is expected to increase in the future.

Microfiltration can be either a flow-through or a cross-flow process. It is largely restricted to use in the pharmaceutical and health sectors but some of the "tighter" cross-flow membranes are being increasingly used in the dairy and paint industries for separation of macro-molecules.

Ultrafiltration has very wide industrial usage (including oil related industry as will be discussed later). It is used:

a. in the paint industry for paint recovery;
b. in the food industry for fruit oil recovery;
c. in the automotive phosphating lines (pre-paint) for phosphate recovery;
d. in the textile industry for dye recovery;
e. in the dairy industry for whole milk, cream and whey recovery;
f. in the pharmaceutical industry for enzyme recovery;
g. in the pulp and paper industry for by-product recovery; and,
h. in municipal and industrial sewage treatment.

Reverse osmosis was developed primarily as a means of providing potable water from brackish and salt water sources. Recent advances in membranes have, however, very greatly expanded the areas of application for this technology. Systems are now in use for:

a. municipal and industrial waste water treatment;
b. product recovery in the pulp and paper industry;
c. dye and solvent recovery in the textile industry;
d. recovery of metal plating wastes;
e. recovery of photographic processing wastes; and,
f. concentration of citrus juices and maple syrup.

Gas separation is, as stated earlier, gaseous phase reverse osmosis. Many of its applications are in the oil patch. Others include:

a. hydrogen recovery from ammonia purge gas; and,
b. hydrogen recovery from methanol purge.

Electrodialysis applications include:

a. reduction of electrolyte content in whey, fruit juice, coffee, milk and sugar in the food industry;
b. recovery of electrolytes from rinse solutions and metal plating baths;
c. ion replacement in organic acids and bases; and,
d. redox chemistry for chlor-alkali and tin.

Applications to the Oil and Related Industries

The objective in all forms of membrane technology is the separation of one or several species from a solution. As such the technology is a branch of separation technology. It is, therefore, not surprising that it has been applied to the oil industry and industries whose processes result in a waste oil product for disposal.

Ultrafiltration (UF) has the capability, especially in the case of tubular membranes to handle liquids with relatively high solids and non-aqueous liquids loadings. It has been in use for a number of years in industries which produce large quantities of water-soluble oils such as gear manufacturers. An example is the General Electric Company plant in Fall River, Massachusetts, USA where over 1900 m^3/yr of soluble oils and other oil contaminated wastes are produced (2). The total concentration of oil is 1-3%, a level which is too high for discharge to the local waterways. An ABCOR ultrafiltration unit was installed in 1973. With this technology, it has been possible to reduce the oil in the discharge water to less than 10 ppm while concentrating the waste oil to over 40%, a level at which it can be used for fuel.

Zenon Environmental Inc. has set up a tubular UF waste oil treatment plant for General Motors in Oshawa (3). In this case, oily wastes, including emulsified oils, are involved. The original 1-2% oil in solution is concentrated with a resultant volume reduction of 80-90%. Flow rates are 10-20 litres per minute. The ultrafiltrate is discharged to the sewers while the concentrated oil is re-used or sent to a waste oil company.

In 1980, ABCOR carried out a short series of tests on the applicability of UF and RO to tar sands process waters (4). Monenco Consultants reviewed the ABCOR data and stated that, at that time, conventional treatment was more appropriate (5). More recent work has been carried out by Zenon (6) and EMR (CANMET) has several studies either under way or planned in this area (7).

Reverse Osmosis has been directly applied to the problem of waste saline water from oil production. In this instance, the technology application has advanced to the point where a US company, ROMEC, has a patent (8).

In the ROMEC system (Figure 3) the saline waste water is drawn from the mud pit, through a filter and oil/water separator to the reverse osmosis (RO) unit. The initial waste water is typical of oil field wastes, a complex mixture of brine, crude oil emulsions, suspended solids, colloidal particles, and a wide range of chemical additives from the drilling and production operations. To deliver the needed quality of water to the RO membrane there are a series of processes for treatment. Stage I is to remove the bulk of the oil. This is done with an oil coalescing system that uses oleophilic baffles that cause the oil to rise to the top where it can be removed. After Stage I, there remains from 15 to 20 ppm of oil in the water. Stage II is an oil adsorbent system which can be a charcoal column or a synthetic product to which oil adheres. Stage III is a two-stage filtration with depth filters using mixing media. The present ROMEC system uses a C.E. Nato product as a pulse bed. Earlier Electromedia by Continental Water has been used. Stage IV is microfiltration in a system using Mott microporous sintered metal filters that filter to 0.2 microns absolute. The submicron filtration operates at from 10 to 35 psi and is fed directly from the mixed media depth filters. Stage V is a chemical injection of about 20 ppm of a chemical blend of proprietary mix that includes antiscalants, antioxidants, chelates and other chemicals. Ideally, the pH is 6 1/2 to 7. The final Stage VI is the RO array of four 4" permeators. Feed is 5 gallons per minute input with about 3 1/2 gallons per minute output. The system takes brine of 35 000 ppm salt and outputs 350 ppm salt.

In addition to the ROMEC system there are a number of experimental and pilot plant RO systems operating in the US oil shale sector. An example of this is the work carried out recently at the University of Kentucky on oil retort waste waters from eastern oil shale (9). This water has characteristics which are similar to other synthetic fuel processes such as: colour, odour, high organics concentration (primarily aliphatic acids, phenols, etc...), NH_3, S^{2-}, high alkalinity, etc... Activated carbon filtration followed by low pressure reverse osmosis was used to treat the water. Rejections of 90% for TOC, Cl^- and S^{2-} were achieved with this system.

Some work has been done in Canada, on the use of RO for Alberta tar sands waste waters and process waters. Work done at the University of Waterloo (10) has shown that 99% salt rejections were possible under laboratory conditions. The feed in this instance was tar sands waste water. Zenon Environmental Inc. has studied the use of RO

on the tar sands waste waters. Very high rejections and high flows were achieved and the study is on-going.

Gas separation (GS) is now fairly widely used in the oil and gas industry and the extent of usage is increasing. Examples given here will cover the range of chemical processing, carbon dioxide fracturing and sour gas cleanup. The chemical process example involves the use of GS membranes in hydrogen recovery at a butamer unit (11) where n-Butane is converted to isobutane, in the unit, in the presence of hydrogen. The off gas contains hydrogen, methane, ethane and propane. This is treated in a GS unit for recovery of hydrogen for re-use in the process. The alkanes are sent to a fractionator.

The carbon dioxide fracturing example comes from the southern USA (12). Large volumes of CO_2 are used in the fracturing of tight formations. The increase in production for fracs has averaged 6 times for oil wells and 3-4 times for gas wells. Average payout time for a CO_2 project was 1 1/2 months. The initial gas contains high concentrations of CO_2 which is removed by GS processing. A modular system is employed since the CO_2 content of the gas decreases with time.

The examples of sour gas cleanup and CO_2 removal come from western Canada (13). With a feed of 14.6% CO_2 at 830 psi (5.72 MPa), a residue or pipeline sales gas was delivered at 2.8% CO_2 and 825 psi (5.68 MPa). Permeate CO_2 concentrations were as high as 63%. Total hydrocarbon loss was about 6.9%. Two years of continuous operation has shown that membrane performance is more than 80% of that at start-up.

At another site with high H_2S and CO_2 feed concentrations, test results look most promising. With a feed of 28% H_2S, 10% CO_2 and 62% ($C_1^+ + N_2$) a single-stage membrane element arrangement delivered a permeate stream of 65% H_2S, 17.4% CO_2, 17.6% ($C_1^+ + N_2$). The residue gas stream was 6.7% H_2S, 5.5% CO_2 and 87.8% ($C_1^+ + N_2$). The next phase in this test is to determine the long-term effects of high-concentration H_2S on membrane permeation efficiency.

EETD Experience Related to Oil Field Liquid Wastes

The Environmental Emergencies Technology Division of Environment Canada has been involved in the field of reverse osmosis and ultrafiltration for 4 years. This involvement has largely been made possible because EETD operates two RO/UF units, a mobile pilot plant and a large laboratory scale unit.

The mobile unit is designed for two purposes:

a) to provide fresh water from salt water for steam cleaning of rocky shorelines in remote areas; and

b) to concentrate dilute aqueous chemical solutions resulting from spills into small bodies of freshwater and chemical landfill leachates.

It also has potential as a means of determining the applicability of reverse osmosis to various industrial effluents.

The unit, which is completely self-contained, is capable of producing from 1800 to 2400 litres per hour of potable water from sea water depending on the membrane used. Its capacity for chemical spill cleanup varies, similarly, with the membrane used and with the concentration and identity of the chemical.

The laboratory scale unit has a capacity of approximately 1000 litres per hour based on salt water. It is functionally similar to the mobile unit and uses the same membrane elements as the larger unit. This laboratory scale unit is used for investigation of membrane capabilities against chemical solutions and as a precursor to the use of the mobile unit in field testing. If EETD assistance has been sought in the remediation of an industrial effluent, spilled chemical or leachate, the laboratory unit is used, if time allows to determine which commercially available membranes are most effective in treating the problem. These membranes are then loaded into the mobile unit and it is sent to the site for extended or short-term trials/remediation. The laboratory scale unit can also be taken to the site and used as a means of further concentrating the concentrate stream produced by the mobile unit.

The mobile unit and a contractor owned unit have been used in several trials which have demonstrated the applicability of RO/UF to problems similar to those faced by the oil industry in dealing with wastes.

The contractor owned unit (used because of its smaller throughput) was used in 1983 to demonstrate the applicability of RO and UF to mud pit wastes (14). Approximately 160 litres (35 gallon) of mud pit wastes were processed by the unit. First the wastes, which contained large quantities of suspended solids, were processed with a UF membrane. The ultrafiltrate (permeate) from the UF membrane was then treated by RO. Table 1 lists the results obtained. It is emphasized that this was a short-term, low volume trial, conducted at low RO pressures, with no attempt to either determine long-term operation of select the optimum membrane for the purpose.

TABLE 1 UF/RO TEST RESULTS

Sample No.	Pressure (PSI)	Permeate Flow Rate US GPM	Feed TDS in (ppm)	Percent Removal					Percent Removal of Water
				TDS*	Ca	Na	Cl	Mg	
1	50-100	1.0-1.25		20.0	99.2	22.9	45.7	-	50
2	100	1.25-1.5		42.3	92.0	22.9	23.9	-	70
3	100	1.0-1.25		47.9	74.0	74.2	19.2	-	70
4	100	1.0-1.25	7 409	N/K	99.3	30.4	Conc.	-	70
5	100	1.0-1.4	7 418	N/K	99.7	Conc.	18.2	-	70
6	100	1.0-1.4	174 440	N/K	99.2	Conc.	0.0	-	70
7	100	1.0-1.4	41 620	N/K	99.9	47.0	Conc.	-	70
Mixed UF concentrates	100	0.75-1.0	26 755	N/K	99.3	Conc.	13.0	-	86
RO of UF Permeate	Start 380 End 285	0.75		89.6	98.2	92.8	47.6	90.0	96

* TDS: total dissolved solids

The mobile unit has been used in a test of cleaning up a spilled wood preservative solution in B.C. (15). This solution, which was very high in chlorophenols, contained sodium tetraborate, wood extracts, sawdust and other fine debris. Subsequent to the spill it had been vacuumed up and stored in railway tank cars awaiting disposal. Using the mobile unit, these wastes and those from a second spill site, were treated by RO. The permeate was suitable for discharge to sewers or the environment and the concentrate at least at the first site, was suitable for re-use. Typical performance, at 34-38 litres per minute, is listed in Table 2.

TABLE 2 RESULTS OF WOOD PROTECTION SOLUTION TREATMENT COMPARISON OF MEMBRANES PERFORMANCE

Total Chlorophenol Concentration (ppm)				Percentage Rejection		
	Permeate					
Tank	Filmtec	DSI	Toray	Filmtec	DSI	Toray
1900	0.445 (1)	1.567	3.337 (2)	99.9	99.9	99.8
735	0.347	1.159	0.565	99.9	99.8	99.9
638	0.174	0.665	2.791 (2)	99.9	99.9	99.6
567	0.073	1.089	6.230 (2)	99.9	99.8	98.9
567	0.201 (1)	0.996	6.16 (2)	99.9	99.8	98.9
290	0.133	0.178	1.668 (2)	99.9	99.9	99.4
218	0.038	0.261	0.434 (2)	99.9	99.9	99.8
156	0.269	0.402	0.009	99.8	99.7	99.9

(1) Leak at membrane due to twisted "0" ring
(2) Damaged membrane

A further trial involving the mobile unit was the cleanup of residual solution from an underground spill of PCB containing organic liquid in Saskatchewan (16). Here the spill had resulted in contaminated ground water which was collected and stored in a tank on the site. 43 000 litres of the contamined water were treated used 2 passes with the RO unit. The result was 40 000 litres of permeate and 3000 litres of concentrate. After analysis, the permeate was discharged to the sewers while the concentrate which had approximately 10% organics as a separate phase was stored for shipment to a US licensed landfill. A savings of $16 000.00 in disposal costs was realized.

The last example involving the mobile unit involves the treatment of an underground plume of sodium chloride in Ontario. This plume is the result of the leaching of road salt from 5% NaCl sand stored in the open and intended for use on roads in the winter. Water from the plume was treated, in a 50 day, 8 hour per day trial. Sodium chloride in the feed was 10 000 to 12 500 ppm while in the concentrate it was 80 000 ppm and in the permeate 200 ppm.

Possible Future Applications of Membrane Technology to the Canadian Oil Patch

There are at least three areas in which it is considered that RO/UF can be used extensively in the oil industry, in Canada. The first of these is the production of drinking water from salt or brackish sources in off-shore and remote operations. This is a well established use of RO.

A second use of UF/RO is in the treatment of mud/waste pit waters. This, as has been previously explained, is an area which has already commenced in the USA. Use of this technology in Canada is, therefore, considered to be simply the application of a proven technology for the amelioration of the environment.

A third example, and again one which has been mentioned earlier, is in the use of UF/RO on tar sands and heavy oil waste and process waters. These are areas in which both Environment Canada and Energy Mines and Resources are currently carrying out testing. It is expected that positive results will be achieved.

Conclusions

Membrane Technology is a rapidly advancing field. It has applicability to many industrial processes including several areas of the oil industry. Its application should result in both improved operations and a better environment.

References

1. Handbook of Separation Techniques for Chemical Engineers, D. C.M. Porter, Annex D, page 1.

2. Ultrafiltration of Soluble Oil Wastes, R.L. Goldsmith, D.A. Roberts and D.L. Burre, Journal of the Water Pollution Control Federation, Vol. 46, No. 9, Sep. 1974, pp. 2183-2192.

3. Membrane & Separation Technology News, Vol. 3, No. 2, Oct. 1984, page 3.

4. Treatment of Waste Produced from Bitumen and Heavy Oil Recovery Wells: An Evaluation of Membrane Processes, ABCOR for AOSTRA, 18 May 1981.

5. Produced Waste Treatment Study - Conventional Treatment, Monenco Consultants Ltd. for AOSTRA, July 1982.

6. Technical and Economic Assessment of the Application of Membrane Technology for Treating Oil/Water/Mineral Emulsions, Zenon Environmental Inc. for CANMET, April 1985.

7. Discussions, Brian Farnand, CANMET, 17 Jan. 1986.

8. United States Patent No. 4,366,063; Dec. 28, 1982.

9. Low Pressure Reverse Osmosis Membranes: Concentration and Treatment of Hazardous Wastes, J.L. Siler and D. Bhattachargys, Hazardous Waste and Hazardous Materials, Vol. 2, No. 1, 1985, pp. 45-65.

10. Synthesis and Transport Properties of Thin Film Composite Membranes II. Preparation of Sulfonated Poly (phenylene Oxide) Thin Film Composite Membranes for Purification of Alberta Tar Sands Waste Waters: RYM Huang and J.J. Kim, Journal of Applied Polymer Science, Vol. 29, 1984, pp. 4029-4035.

11. Results Confirm Membranes H_2 Recovery Role, Anonymous, Oil and Gas Journal, Oct. 28, 1985, page 121.

12. Take Care in Picking Membranes to Combine with Other Processes for CO_2 Removal, R. Schendel and J. Seymour, Oil and Gas Journal, Feb. 28, 1985, pp. 84-86.

13. Membranes for Natural Gas Sweetening, W.H. Mazur and M.C. Chan, Chemical Engineering Progress, Oct. 82, pp. 38-43.

14. Water Recovery from Drilling Fluids Using UF/RO Membranes, H. Whittaker, Spill Technology Newsletter, Vol. 8(5), Sept.-Oct. 1983, pp. 109-111.

15. Reverse Osmosis for Cleanup of Spilled Wood Protection Solution, J.B. Straforelli and H. Whittaker, Proceedings of the Technical Seminar on Chemical Spills, Feb. 5-7, 1985, pp. 254-270.

16. Cleanup of PCB Contaminated Groundwater by Reverse Osmosis, H. Whittaker and R. Clark, op cit, pp. 229-237.

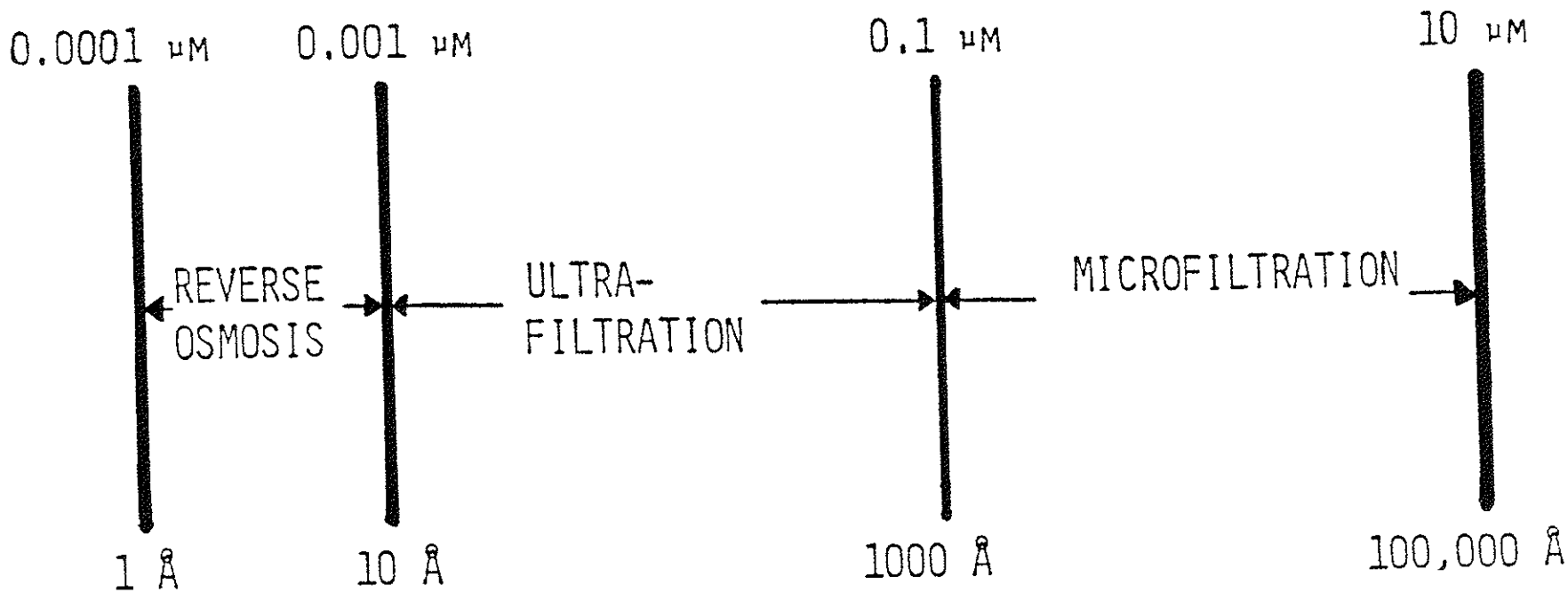

FIGURE 1 PARTICLE SIZE REMOVAL RANGES FOR BASIC PROCESSES

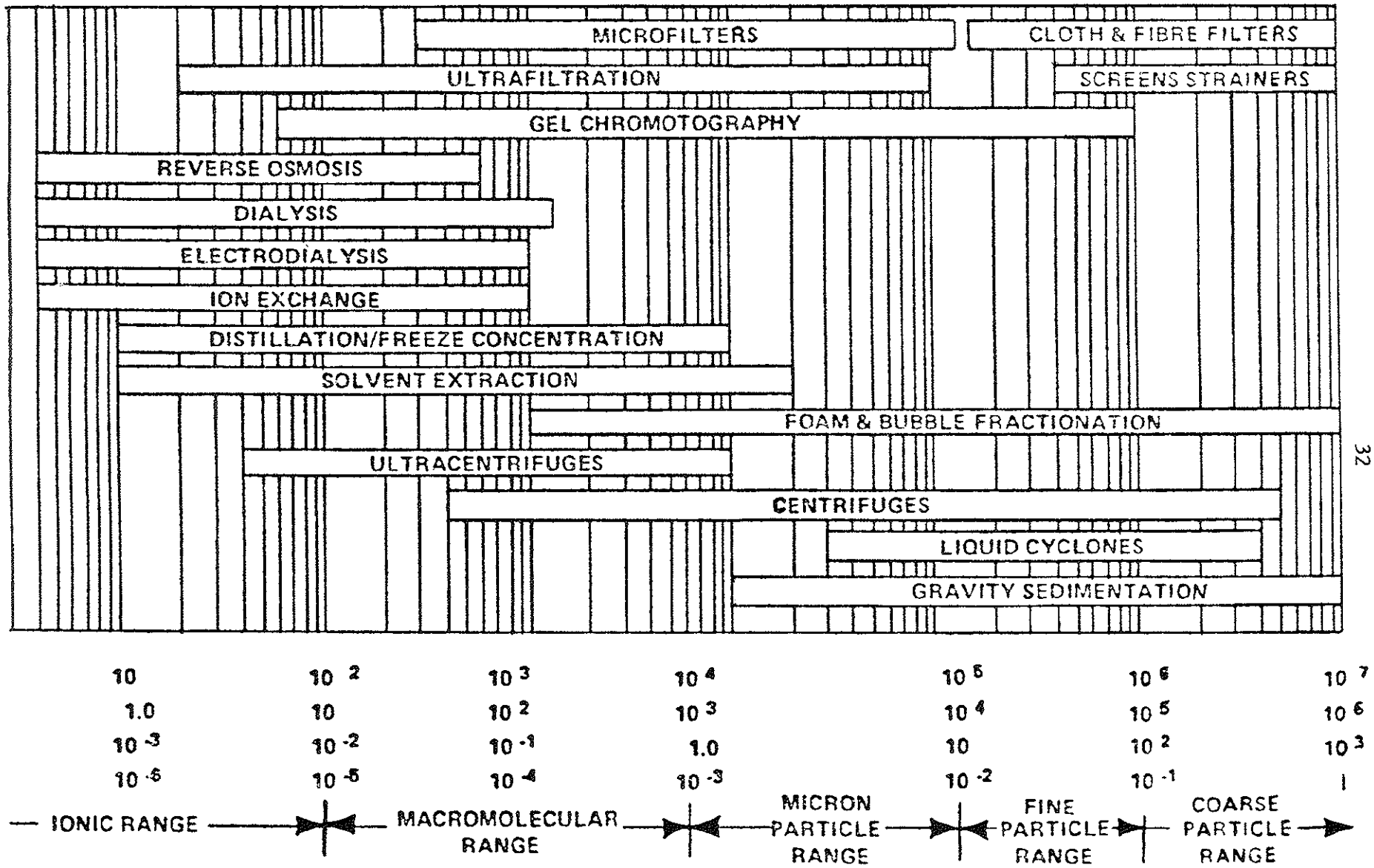

FIGURE 2 PARTICLE SIZE RANGES FOR A VARIETY OF SEPARATION PROCESSES

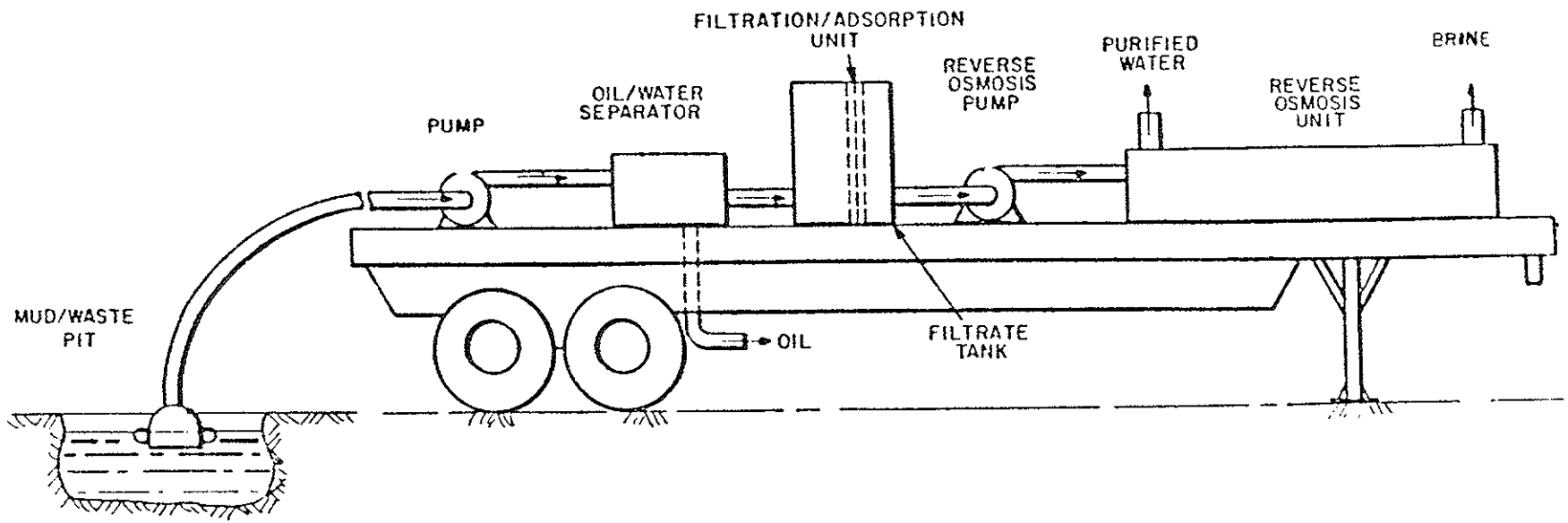

FIGURE 3 ROMEC SYSTEM FOR TREATING DRILLING MUDS

RECENT PETROLEUM DISPERSIBILITY RESULTS

Submitted by: Mervin Fingas, Mark Bobra and John Doran
Environmental Emergencies Technology Division
Environmental Protection Service
Environment Canada
Ottawa, Ontario

The ease with which a petroleum product disperses into the water column is very useful information to have when responding to a spill. Natural dispersion is the degree to which a product disperses by itself under various environmental conditions. The amount that disperses is important for the understanding of the aquatic toxicity, and also for estimating the amount remaining for countermeasures or for impact on resources or adjacent shoreline. Chemical dispersibility is the degree to which the oil is removed from the surface into the water column with the aid of a chemical agent, commonly known as a dispersant. Chemical dispersibility of an oil is important for assessing its potential effectiveness as a countermeasure technique.

Both chemical and natural dispersibility are difficult to measure because many factors such as wind speed, temperature, sea state and salinity are known to influence the final results. We have used the controllable and repeatable energy level feature of the Mackay Nadeau Steelman (MNS) apparatus to obtain values that can be used by the oil spill community to gauge oil dispersibility, recognizing that the values obtained are only true for the sea condition simulated by that apparatus. This device employs a high-velocity stream of air to energize six litres of water.

The test oil is placed in a small containment ring after the wave condition is stabilized. It is then released, and left for ten minutes. A water sample is then taken and analyzed to provide an effectiveness value. The MNS device has become a standard in Canada as well as in other countries (1,2). A number of problems have been identified with this test methodology (for example, the high energy regime that it simulates), however, of the very few alternatives available, it is considered to be the best for our purposes (3).

Recent test results are presented in Table 1. The test oils include a number of crude oils as well as some refined products. In addition, some oils were retested after weathering and the volumetric evaporative loss in percentage is given. The data are measured at standard conditions for the MNS apparatus as noted in the references, including a 30 o/oo salinity and the temperature being set to either 0°C or 15°C as noted

TABLE 1 DISPERSABILITY RESULTS

	Percent Dispersed Into Water Column			
	Blank Run (Natural Dispersibility)		Chemical Dispersibility (With Corexit 9527)	
Oil Type	0°C	15°C	0°C	15°C
Adgo	63	20	92	96
Adgo (2.6% evaporated)	1	10	88	74
Amauligak	50	15	93	71
Amauligak (13.4% evaporated)	13	28	83	65
Amauligak (19.4% evaporated	22	6	74	67
Automotive Diesel	7	5	92	94
Automotive Gasoline	38	38	54	46
Bent Horn	2	5	86	68
Bent Horn (20.4% evaporated)	0	0	12	80
Bent Horn (32.9% evaporated)	0	9	0	69
Bunker C	0	0	0	3
Electrical Lubricating Oil	4	14	49	28
Electrical Transformer Oil	21	21	72	94
Fuel Oil No. 2	26	24	86	75
Hibernia	0	0	10	48
Hibernia (18.2% evaporated)	0	0	4	46
Hibernia (23.0% evaporated)	0	0	0	19
Issungnak	0	34	16	91
Issungnak (15% evaporated)	0	0	0	99
Issungnak (25% evaporated)	0	0	0	85
Lagomedio	1	2	73	81
Lagomedio (8.8% evaporated)	1	5	62	69
Lagomedio (14.8% evaporated)	0	2	20	85
Norman Wells	5	8	79	75
Tarsiut	38	30	76	81
Tarsiut (12.4% evaporated)	16	22	57	53
Tarsiut (16.4% evaporated)	17	39	62	72
Transmountain Blend	0	1	40	84
Transmountain Blend (18.5% evaporated)	0	0	0	80
Transmountain Blend (28.5% evaporated)	0	0	0	83

in the table. The blank run is taken to be an indicator of natural dispersibility as shown in the first two columns of the table. In this test, the MNS apparatus is operated as usual but no dispersant is added to the oil before release in the apparatus. In the case of the chemical dispersibility tests, a constant dispersant dose equivalent to an oil:dispersant ratio of 20:1 was added. The dispersant in every case was Corexit 9527, an Exxon product.

The work has led up to a number of observations or generalizations as follows:

1. Dispersibility, whether it be natural or chemical, is very much a function of oil type. Correlation to obvious data such as viscosity, density, etc. is poor and thus a complex model including oil-specific parameters such as paraffin content, is necessary to predict dispersibility.
2. Many of the Beaufort crude oils such as Adgo, Amauligak, and Tarsiut are very readily dispersed, both naturally and chemically.
3. High paraffin oils such as Hibernia and Bent Horn are not readily dispersed by either natural or chemical means.
4. Some oils appear to disperse better at lower temperatures. During the experiments this was observed to be due to the viscous shearing of large oil drops into the water column. Most oils showed the reverse tendency.
5. There is a viscous cut-off point where an oil becomes so viscous that dispersant will not mix with it. This effect can be seen in the case of Bent Horn and Transmountain oils where the increased weathering and thus the increased viscosity resulted in a dramatic drop-off in dispersant effectiveness.

References

1. Guidelines on the Use and Acceptability of Oil Spill Dispersants, Environmental Protection Service Report EPS 1-EP-84-1, Ottawa, Ontario, 1984.

2. Mackay, D. and F. Szeto, Effectiveness of Oil Spill Dispersants - Development of a Laboratory Method and Results for Selected Commercial Products, Institute for Environmental Studies Report No. EE-16, University of Toronto, Toronto, Ontario, 1980.

3. Mackay, D., A. Chau, K. Hossain and M. Bobra, "Measurement and Prediction of the Effectiveness of Oil Spill Dispersants" in Oil Spill Chemical Dispersants: Research, Experience and Recommendations, STP 840, Tom E. Allen, Ed., American Society for Testing and Materials, Philadelphia, Pennsylvania, 1984, pp. 38-54.