

The methods listed here are those used by the Emergencies Science Division of Environment Canada. In some cases, both new and old methods are described, as data from both may be included in the catalogue.

Sample Collection and Storage

The bulk oil container is mechanically mixed prior to obtaining a working sample. Large drums (205-L) are mixed for 24 hours; 20-L cans are mixed for three hours. Working samples are stored in 2-L high-density polyethylene bottles with polypropylene screw closures (Nalgene, Rochester, NY). When not in use, all working samples are stored in a temperature-controlled room at 5°C. The working sample is shaken for 30 minutes prior to removing an aliquot for testing.

Evaporation (Weathering) of Oils

Prior to 1993, evaporated oils were produced by bubbling air up through a 1-L graduated cylinder filled with oil as per the method developed by Stiver and Mackay (Stiver 83). For oils evaporated by this method, the evaporative loss is expressed as a volume percent. For most light to medium crude oils, this method was used to produce two evaporated oil samples representative of light and moderate degrees of evaporation respectively.

In 1993, a new method for bulk evaporation was developed. Rotary evaporation of crude oils can produce a greater degree of evaporation in a shorter period of time, allowing the production, for most light to medium crude oils, of three evaporated oil samples representative of light, moderate, and heavy degrees of evaporation. The apparatus used is a Wheaton N10 rotary evaporator with a 10-L flask and an integral water bath. The bath temperature can be controlled to $\pm 0.5^\circ\text{C}$. The temperature control range is 1°C to 120°C . The speed of rotation can be continuously varied from 10 to 135 rpm.

- a) The water bath is filled with distilled water and brought to 80°C . Higher temperatures are avoided to ensure that cracking of oil components does not take place. The temperature should remain constant throughout the evaporation process.
- b) The oil is removed from storage and shaken for 30 minutes. Two litres of oil is placed into the tared 10-L flask.
- c) The flask is placed on the evaporator and run at full speed (135 rpm). An air flow of approximately 13 L/min through the flask is maintained by leaving the vacuum release stopcock open to atmospheric pressure while a small vacuum pump is running.
- d) The flask is reweighed every half hour for the first hour, every hour up to eight hours, every two hours up to 16 hours, every four hours up to 32 hours, and finally at 48 hours. This produces a heavily evaporated oil. For light and medium oils, two more evaporated oils are produced having appropriate intermediate mass losses. For heavy oils, fewer intermediate samples can be produced. All intermediate evaporated oils are produced in the same way as the 48-hour sample, but over a shorter time period, and with only initial and final weight measurements.
- e) If evaporation must be stopped (e.g. scheduled power or water outage, overnight, weekends), the flask must be sealed tightly and refrigerated. When the run is restarted, the flask should be removed from the cold and allowed to sit at room temperature while the water bath is returned to operating temperature.

Equation(s) for Predicting Evaporation

The evaporation rate of each oil is determined by measuring weight loss over time, using an electronic balance capable of weighing to 0.01 g. The weight is recorded using a system consisting of a computer, data acquisition software, and serial links to the balance. Data are recorded using a sequence with a time multiplier of 1.1 to ensure that approximately equal weight intervals are recorded. Measurements are conducted in the following fashion. A glass petri dish (139 mm i.d.) is tared, then loaded with approximately 20 g of oil. Data acquisition is started and continued until the desired time (varying from a few days for light oils to several days for heavy oils).

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Vessels are cleaned with dichloromethane and dried before a new experiment is started. Measurements are conducted in a controlled-temperature chamber at 15°C. Temperatures are verified with a digital thermometer.

Data are recorded and plotted so that a curve fit can be produced. The weight percent equations are determined without the use of a constant parameter.

Sulphur

Sulphur contents from EETD and ESD were determined using a Horiba MEA 200 sulphur and chlorine analyzer, in accordance with ASTM method D 4294, *Standard Test Method for Sulfur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectroscopy* (ASTM D 4294).

Water Content

Water contents are determined by Karl Fischer titration, as in ASTM method D 4377, *Standard Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration* (ASTM, D 4377) with the following modifications. A Metrohm 701 KF automatic titrator is used, and the sample is dissolved in a pre-titrated 1:1:2 volume mixture of methanol/chloroform/toluene. Samples are run in duplicate, and the mean water content is reported.

Flash Point

A SUR BERLIN TAG 2 automatic flash point tester, which has been modified by adding a stirring mechanism, is used to determine flash points. The mechanism operates in a similar fashion to a Pensky-Martens tester, but is of a more efficient design. The stirrer aids in producing more uniform heat transfer to oils that exceed the design viscosity, and in no way interferes with the test mechanism. The oil is shaken for 30 minutes and then ASTM method D 56 is followed. Samples are run in duplicate and the mean flash point is reported.

Reid Vapour Pressure

Reid Vapour Pressure data from EETD and ESD are measured in accordance with ASTM method D 323- *Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method)*, (ASTM D 323)

Pour Point

- a) If the oil is not fluid at the storage temperature, it is warmed until fluid and then shaken briefly by hand. Otherwise, the oil is removed from cold storage and shaken for 30 minutes.
- b) The oil is poured into test jars meeting the specifications of ASTM method D 97. (ASTM D 97) Duplicate samples of each oil are tested.
- c) The test jars are fitted with stoppers and ASTM designated thermometers, and warmed in a water bath to 50°C.
- d) The samples are removed from the bath and cooling takes place in the following manner:
 - i) The samples are allowed to cool to room temperature.
 - ii) If additional cooling is required, the samples are moved sequentially to a cold room maintained at 5°C, a freezer at -25°C, and finally to an acetone/dry ice bath at approximately -65°C.
- e) As the sample is cooling, it is checked periodically to see if the pour point has been reached. These checks are made as per ASTM method D 97, but not necessarily at intervals which are multiples of 3°C.
- f) When the pour point has been reached, 3°C is added to the temperature recorded from the thermometer, as specified in the ASTM method. This value is reported as the pour point.

Density

Density is measured using an Anton Parr DMA 48 digital density meter, and following ASTM method D 5002 (ASTM D 5002). Samples are run in duplicate and the mean value is reported.

Viscosity

Dynamic viscosity data are determined using a HAAKE RV20 Rotovisco with the M5 measuring system, SV1 and NV sensors, and HAAKE RC20 Rheocontroller.

- a) The sample is removed from cold storage and shaken for 30 minutes.
- b) A rotor and cup are chosen based on visual observation of the oil sample after shaking.

Sensor (rotor)	NV	SV1
Cup	NV	SV
Application	Low viscosity	High viscosity
Viscosity range (cP)	1 - 10^4	50 - 10^6
Volume (mL)	9	9

- c) Using a 10-mL disposable syringe, an aliquot of oil is obtained. If the oil is too viscous to be pulled into the syringe, it may be sampled by removing the plunger, cutting off the end of the syringe, and plunging the syringe into the oil. The excess oil is wiped off from the outside of the syringe and the sample cup is carefully filled.
- d) The sample cup is placed into the holding container. A visual check is made to determine if there is sufficient sample (up to the top of the rotor) or excess sample (over the top of the rotor). The amount of sample is adjusted as necessary.
- e) The sample is allowed to equilibrate at the chosen temperature; 15 minutes at 15°C and 25°C, or 30 minutes at 0°C.
- f) The measurement parameters are set:

Shear rate: For newtonian oils, a shear rate is chosen that will most accurately measure the viscosity. In most cases, this will be 100/s for the SV1 rotor and 1000/s for the NV rotor. Non-newtonian oils are run at 1/s, 10/s, and 100/s whenever possible.

Ramp program: Ramp up, 5 minutes. Hold, 5 minutes. Ramp down, 5 minutes.
- g) When the run is complete, the data are printed out along with a plot of viscosity versus shear rate.
- h) The rotor and cup are removed and cleaned using sorbents and dichloromethane.
- i) Two separate runs are performed for each viscosity measurement, and the mean is reported. For non-newtonian oils, one measurement is made for each shear rate and the reported value is the viscosity measured at the start of the 5-minute hold during the ramp program.

Emulsion Formation

Water-in-oil emulsions are formed at 15°C, in 2.2-L fluorinated vessels on an end-over-end rotary mixer at a nominal rotational speed of 50 rpm.

- a) 600 mL of salt water (3.3% w/v NaCl) is placed in each mixing vessel.
- b) 30 mL of oil is added to each vessel for a 1:20 oil:water ratio.

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- c) The vessels are sealed and placed in the rotary mixer such that the cap of each mixing vessel follows, rather than leads, the direction of rotation. The rotary mixer is kept in a temperature-controlled cold room at 15°C. The vessels and their contents are allowed to stand for approximately 4 hours before rotation begins, then mixed continuously for 12 hours.
- d) At the conclusion of the mixing time, the emulsions are collected from the vessels for measurement of water content, viscosity, and the complex modulus. The emulsions are stored in the cold room at 15°C for one week, then observed for changes in physical appearance. Stability type is assigned based on the observations and data.

Measurements

Emulsion water content is performed as described previously, by volumetric titration using the Karl-Fischer reaction, with potentiometric end-point determination.

The viscosity at 15°C is measured on a RV20 Rotovisco with M5 measuring head, RC20 rheocontroller and dedicated software package, using SV1 spindle and SV cup (cylindrical geometry). The shear rate is 1/s.

The complex modulus, also referred to as the 'stiffness' modulus, is a measure of the overall resistance of the material to flow under an applied stress, in units of force per unit area. It combines the viscosity and elasticity components of a visco-elastic material, such as a water-in-oil emulsion, into a single measure by vector addition. Since crude oils generally do not possess significant elasticity, it has been found that dividing the complex modulus of the emulsion by the viscosity of the fresh oil is a useful indicator of the stability of the emulsion, as a ratio greater than 200 generally indicates a stable emulsion. The complex modulus is measured on a RS100 RheoStress rheometer using a 35-mm plate-plate geometry. A stress sweep is performed in the range of 25 to 1,000,000 mPa in the oscillation mode at a frequency of 1 Hz. The resulting complex modulus in the linear portion of the range is reported.

Chemical Dispersibility

The working sample is shaken 30 minutes prior to removing an aliquot for testing. For dispersant testing, an aliquot is removed as needed from the working sample and stored in a 40-mL glass vial with a Teflon-lined cap.

- a) Premix sample preparation

Weigh approximately 1.0 mL of oil into a 5-mL amber vial with Teflon-lined cap. Add approximately 100 mg of dispersant into the oil. Add oil until a 1:25.0 ratio of dispersant to oil is achieved (approximately 2.5 mL oil in total). Mix well by shaking manually.

- b) Salt-water preparation

Weigh out salt and add lab water to obtain a 3.3% (w/v) solution.

- c) Swirling flask preparation

Measure 120 mL of salt water into a 125-mL modified Erlenmeyer flask. Insert the flask into the flask holders on the oscillating table of the shaker. Using a positive displacement pipette, carefully apply 100 µL of pre-mix solution onto the surface of the water by touching the tip of the pipette to the surface and gently expelling the oil/surfactant mixture.

- d) Shaking of swirling flasks

The flask and contents are mechanically mixed on the shaker with the temperature-controlled-chamber at 20°C. A rotation speed of 150 rpm and a mixing time of 20 minutes is used to agitate the samples followed by a 10-minute settling period.

e) Sample collection

Drain 3 mL of the oil-in-water phase to waste, eliminating any oil from the spout of the flask. Collect a 30 mL aliquot in a graduated cylinder and transfer to a 125-mL separatory funnel. Extract with 3 x 5 mL of a 70:30 volume % dichloromethane:pentane solvent mixture, collected in a 25-mL graduated mixing cylinder and topped up to 15 mL.

f) Sample analysis

Prior to 1994, sample analysis was done using UV/VIS spectroscopy. A semi-micro, UV/VIS cell is filled with a portion of the extract and its absorbance measured at 340 nm, 370 nm, and 400 nm. The absorbance of the samples is compared to a calibration curve derived from the absorbance of a series of prepared oil-in-solvent standards (see below) to produce percent efficiency results.

Since 1994, sample analysis consists of gas chromatographic analysis of the resolved petroleum hydrocarbon (RPH) peak area using a flame ionization detector (GC/FID) to determine the concentration of oil in solvent. A 900.0 μ L portion of the 15 mL solvent extract and a 100.0 μ L volume of internal standard (200 ppm 5- α -androstande in hexane) are combined in a 12 mm x 32 mm crimp-style vial with aluminium/Teflon seals and shaken well. Petroleum hydrocarbon content is quantified by the internal standard method using the total resolved peak area of the chromatogram and the average hydrocarbon response factor determined over the entire analytical range:

$$\text{RPH} = A_{\text{total}} / A_{\text{IS}} \times \text{RRF}^{-1} \times 20 \text{ (mg)} \times 15 \times 120/30/0.9 \quad (1)$$

Where:

RPH is the resolved petroleum hydrocarbon

A_{total} is the total area of the resolved peaks in counts

A_{IS} is the area of the internal standard

RRF is the relative response factor for a series of alkane standards covering the analytical range

g) Calibration standards

A series of 6 oil-in-solvent standards are prepared for evaluating the efficiency of the dispersant for each dispersant/oil combination. The volume of premixed dispersant/oil solution for each standard is selected to represent a percentage efficiency of the dispersed oil, for example, 50 μ L = 50% efficiency (see Step(h) below for method of choosing calibration standard volumes). The dispersant/oil mixture is then accurately measured and applied to the water surface, and treated in the same manner as the samples (see Step (d) above). At this point, the entire volume of water is transferred to a 250-mL separatory funnel and extracted with 3 x 20 mL of a solvent mixture of 70:30 volume % dichloromethane:pentane. All oil is extracted, including the oil slick and oil on the walls of the swirling flask test vessel, using the volume of extraction solvent to rinse the flask of remaining oil before adding to the separatory funnel. The extracts are combined in a graduated cylinder and topped up to a total volume of 60 mL.

Chromatographic analysis is then performed consistent with the sample analysis (see Step (f) above). A calibration curve of RPH versus % efficiency is produced using a graphics software package. From a comparison of the calibration curve to the RPH content of the samples, the % efficiency is calculated.

$$\text{RPH} = A_{\text{total}} / A_{\text{IS}} \times \text{RRF}^{-1} \times 20 \text{ (mg)} \times 60 \times 120/120/0.9 \quad (2)$$

Where:

RPH is the resolved petroleum hydrocarbon

A_{total} is the total area of the resolved peaks in counts

A_{IS} is the area of the internal standard

RRF is the relative response factor for a series of alkane standards covering the analytical range

h) Selecting the volume range of the calibration standards

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The volumes of the six calibration standards are chosen such that the RPH determined for each of the six samples of each dispersant/oil combination fall within the RPH range of the standards. The following guide is used to determine the range of standards for each type of oil being dispersed:

Heavy oil - 10, 15, 20, 25, 30, 35%

Medium oil - 10, 20, 30, 40, 50, 60%

Light oil - 30, 40, 50, 60, 70, 80%

i) Gas chromatograph parameters and sequencing

Petroleum hydrocarbon analysis for C₈ through C₄₀ n-alkanes of the dispersed oil-in-water is carried out by high resolution capillary GC/FID under the following conditions:

Column	30 m x 0.25 mm ID HP-5 fused silica column (0.10 mm film thickness)	
Detector	Flame ionization detector	
Autosampler	Hewlett Packard 7673	
Inlet	Splitless	
Gases	Carrier – helium	1.6 mL/min, nominal
	Make-up – helium	28.4 mL/min
	Detector air	400 mL/min
	Detector hydrogen	30 mL/min
Injection volume	1 µL	
Injector temperature	290°C	
Detector temperature	320°C	
Temperature program	50°C for 1 minute, 15°C/min to 310°C, hold 5 minutes	
Daily calibration	Alkane standard mixture of 20 ppm (5- α -androstane, alkane mix, o-terphenyl in hexane) is measured before and after each sample set.	

Hydrocarbon Groups

Saturates, Aromatics, Resins, and Asphaltenes

- 25 mL of n-pentane is added to 2 g of oil, stirred, and allowed to stand for 30 minutes at room temperature. The asphaltenes are then removed by vacuum filtration through a 0.45 µm membrane, and the pentane is recovered by rotary evaporation at 30°C, leaving the maltenes.
- 0.4 g to 0.5 g of maltenes is placed on an open glass column (400 mm x 19 mm I.D. x 22 mm O.D., fritted, with stopcock) packed with 30 g silica, topped with 1.5 cm anhydrous sodium sulphate, and saturated with hexane.
- The sample is eluted with 100 mL hexane and 100 mL of eluant is collected and labeled as 'saturates'.
- The sample is eluted with 100 mL hexane/benzene (1:1) and 100 mL of eluant is collected and labeled as 'aromatics'.
- The sample is eluted with 100 mL methanol and 100 mL of eluant is collected and labeled as 'resins'.
- The sample is eluted with 100 mL dichloromethane and the eluant is collected and labeled as 'resins'.
- Rotary evaporation is used to recover the bulk of the solvents, followed by nitrogen blow down.
- Each hydrocarbon group is weighed after solvent recovery is complete. The weights of the two resin fractions are combined.

If the oil used has an initial boiling point (IBP) above 250°C (determined by simulated distillation), a good mass balance can be obtained (>95%). However, most fresh crude oils will have an IBP well below 250°C, and the loss of light ends during solvent recovery results in a poor mass balance. Fortunately, by making the reasonable assumptions that a) resin and asphaltene contents are not affected by evaporative losses, and b) the aromatic

portion of the lost light ends can be equated to the BTEX plus C₃-benzenes content, it is possible to calculate the correct distribution of hydrocarbon groups. Samples are run in duplicate and the mean is reported.

Waxes

Gas Chromatographic Method

The saturate fraction of an oil is obtained as described above and analyzed using the same instrument and operating conditions as described in **Boiling Point Distribution** below. The resulting chromatogram is integrated first to obtain the total area, and then a second time to obtain the resolved C₁₈₊ area. The ratio of the resolved area to the total area is then used to calculate the wax content of the oil. Additional details of the method, including a sample calculation, can be found in Jokuty 97.

Gravimetric Method

- a) Add 50 mL of n-pentane to a 5-mL sample of oil, let stand for 30 minutes, then remove the precipitated asphaltenes by vacuum filtration through a 0.45- μ m membrane .
- b) Remove the n-pentane by rotary evaporation at 30°C.
- c) Transfer the deasphalted oil into a 250-mL Teflon Erlenmeyer flask using 50 mL of a 1:1 volume mixture of dichloromethane (DCM) and methyl ethyl ketone (MEK). The flask is stoppered and swirled for ½ hour.
- d) Weigh a Buchner funnel to 0.0001 g. Chill the funnel, the Teflon flask, the filtering flask, and a squeeze bottle of DCM/MEK at -30°C.
- e) Before filtering, weigh a Whatman GF/C 5.5-cm glass microfibre filter to 0.0001 g.
- f) Working as quickly as possible, set up the chilled filtering apparatus. Turn the vacuum pump on at maximum, and wet the filter with the chilled DCM/MEK solution.
- g) Taking extra care to pour the solution into the centre of the filter, filter the oil solution quickly to avoid warming and possible dissolution of the precipitated waxes.
- h) Rinse the Teflon flask with chilled DCM/MEK which is then poured onto the filter.
- i) Continue aspirating for five minutes, then obtain a final weight.

Samples are run in duplicate and the mean is reported.

Adhesion

This method requires the use of an analytical pan balance capable of weighing to 0.0001 g, and with provision for weighing from below the pan. Some type of draft shield will probably be required to obtain stable readings. Also required is a standard penetrometer needle as described in ASTM method D 5 - *Standard Test Method for Penetration of Bituminous Materials* (ASTM D 5), adapted for hanging below the balance.

- a) The oil sample is allowed to stand at room temperature for 30 minutes.
- b) The sample bottle is shaken for 30 minutes using the reciprocating shaker.
- c) The balance is prepared for measurement by hanging a penetrometer needle, for which the surface area of the stainless steel section has been calculated, from the balance hook and allowing the weight to stabilize. The weight of the clean needle is recorded.
- d) Approximately 80 mL of oil is poured into a 100-mL beaker. The beaker is elevated, using a lab jack, until the top of the stainless steel needle meets the top of the oil. Care must be taken to avoid having the oil

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creep up onto the brass section of the needle, as the surface area calculation is based only on the stainless steel portion.

- e) The needle is left in the oil for 30 seconds, and then the beaker is lowered, allowing the needle to hang undisturbed.
- f) After 30 minutes, the weight of the needle plus oil is recorded.
- g) The needle is cleaned with dichloromethane and allowed to dry before the measurement is repeated. A minimum of four measurements are made for each oil. The same beaker of oil can be used for all measurements.
- h) The oil adhesion is calculated as the average weight of oil remaining on the needle divided by the needle's surface area.

Volatile Organic Compounds

BTEX plus C₃-substituted benzenes are measured by ESD using gas chromatography with mass spectrometric detection (GC/MS). Details of the method are given in Wang 95.

Surface Tension and Interfacial Tension

Prior to 1994, surface and interfacial tensions were measured using a CSC manual DuNouy ring tensiometer in a temperature-controlled room. Since 1994, surface tension and interfacial tension are measured using a Kruss K10ST automatic DuNouy ring tensiometer with cooling bath. The instrument is operated according to the manufacturers instructions, with one modification. Ordinary 100-mL Pyrex beakers are used instead of the special sample containers supplied by Kruss.

The beakers are prepared for use by rinsing with dichloromethane, followed by soaking and washing with a commercial cleaner (Decon 75), and thorough rinsing with water purified by reverse osmosis. The beakers are then oven-dried at 160°C, cooled to room temperature, and stored at the desired measurement temperature.

The procedure for making a measurement is essentially that found in ASTM method D 971, but the raising of the platform is done automatically by the instrument, and sample temperature is also maintained automatically. Calculation of the interfacial tension is done as described in the ASTM method (ASTM D 971). Samples are run in duplicate and the mean is reported.

Boiling Point Distribution

This analysis is performed with an AC Analytical Controls SIMDIS analyzer, comprised of a Hewlett Packard 5290 Series II gas chromatograph with an Analytical Controls Programmable Temperature Vaporizer (PTV) injector. The system uses a special high-temperature column which is aluminum-clad, fused silica, 5 m x 0.53 mm diameter, and has 0.09 µm phase thickness. Sub-ambient cooling is provided by liquid nitrogen. Reference oil samples and calibration mixtures are run according to the AC 750 method provided by analytical controls.

- a) Samples are made up as 2% solutions (by weight) of whole crude oil in carbon disulphide (CS₂). Injection volume is 0.5 µL.
- b) The carrier gas used is helium at a flow rate of 19 mL/min.
- c) The injector temperature program runs from 40°C to 430°C at 70°C per minute.
- d) The oven temperature program runs from -20°C to 430°C at 10°C per minute, with a three minute hold at 430°C.

The flame ionization detector operates at 430°C.

Metals

To overcome problems inherent in the direct analysis of xylene solutions by ICP/AES, a method was developed at ESD using microwave digestion of oils with nitric acid (Cao 92; Fingas 95b).

Aqueous Solubility

10 mL of oil were placed on top of 100 mL of fresh water in a 125-mL separatory funnel. This was allowed to stand for one week, in the dark, at room temperature. The analysis was done by purge and trap using a Hewlett-Packard 5890 Gas Chromatograph (FID) with a Tekmar 4000 Dynamic Headspace Concentrator. A trap containing 3% SP-2100/Chromosorb W Aw and Tenax TA (Supelco) was used, together with the following parameters:

Tekmar 4000

Purge pressure	20 psi
Purge gas (helium) flow	40 mL/minute
Purge time	12 minutes
Desorb time	4 minutes
Bake time	17 minutes
Line temperature	115-120°C
Valve Temperature	115-120°C

Gas Chromatograph

Initial temperature	40°C
Initial time	10 minutes
Heating rate	6°C/minute
Final temperature	250°C
Final time	20 minutes
Detector temperature	300°C