

**EXTRACTABLE PETROLEUM PRODUCTS
(AND RELATED LOW VOLATILITY ORGANIC COMPOUNDS)**

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1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of low volatility petroleum products and organic compounds that are extractable and soluble in moderate to low polarity organic solvents and are amenable to gas chromatography.

1.2 The method includes the determination of compounds listed in Table 1 in a liquid or solid matrix. The estimated quantitation limits are also listed in Table 1.

2.0 SUMMARY OF METHOD

2.1 A 1-liter sample of liquid or 30-gram sample of solid is extracted. The extract is dried and concentrated. A flame ionization capillary gas chromatography method is used to quantitate the compounds or mixtures of interest; a gas chromatograph/mass spectrometer/data system may also be used.

2.2 Figures 1 to 4 show the chromatograms of some of the more common analytes of interest. Identification of various petroleum products is performed by comparison of the chromatograms of samples and commercial products, preferably utilizing computer data system overlay. The commercial products are used as standards for quantitation.

2.3 This method is based in part on USEPA methods 8000 and 8100, SW-846, "Test Methods for Evaluating Solid Waste," 3rd Edition.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 11.4.

3.1.1 Scrupulous cleaning of glassware and other equipment is necessary to avoid contamination and carryover. Glassware, sonicator probes, and other items used in sample preparation should be thoroughly detergent washed, rinsed with tap water and distilled water, solvent rinsed, and dried prior to use. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all glass systems or purchase of high purity solvent grades (Ultra, Omnisolv, Nanograde, etc.) may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

3.3 Petroleum products are complex mixtures of compounds derived from crude petroleum, and different products may have overlapping boiling ranges and chromatograms. The products are also subject to degradation in the environment with consequent changes in chromatographic profile.

4.0 SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method.

5.0 APPARATUS AND MATERIALS

5.1 Gas chromatograph

5.1.1 Analytical system complete with gas chromatograph suitable for a capillary column and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.1.2 Column - J & W DB-5 fused silica capillary column or equivalent, 30 meter x 0.32mm ID, 1 micron film thickness.

5.1.3 Detector - Flame ionization. If GC/MS is used, the total ion chromatogram may be used in place of the FID chromatogram.

5.2 Volumetric Flasks: 10-,50-, and 100-mL, ground glass stopper.

5.3 Microsyringes - 10- μ L, 25- μ L, 50- μ L, 100- μ L.

6.0 REAGENTS

6.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at the MDL of each parameter of interest.

6.2 Acetone, methanol, methylene chloride, 1,1,2-trichloro-1,2,2-trifluoroethane -- Pesticide quality or better.

6.3 Stock standard solutions (10.00 µg/µL)--Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.3.1 Prepare stock standard solutions by accurately weighing about 0.100 g of pure material. Dissolve the material in pesticide quality methylene chloride, dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst.

6.3.2 Transfer the stock standard solutions into Teflon-sealed crimp-top vials. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.3.3 Stock standard solutions must be replaced after six months, or sooner if degradation, solvent loss, or other problem is indicated.

7.0 CALIBRATION

7.1 Establish gas chromatographic operating conditions to produce good separation of any individual peaks and good definition of shape, maximum response, and initial rise from baseline and final descent to baseline in order to distinguish a variety of products, possibly of overlapping boiling range. Figures 1 to 4 may serve as examples.

7.2 External standard calibration procedure.

7.2.1 Verification of the identity of the contaminant must be established by comparison of sample chromatograms with high-quality commercial products used as standards. Petroleum products are complex mixtures of compounds derived from crude petroleum, and different products may have overlapping boiling ranges and chromatograms; care must be taken to distinguish closely related products and to account for possible degradation in the environment. If the identity of the product is not known, identification is performed by comparison of the chromatograms of samples and various commercial products. Guidance for this comparison process is contained in references such as ASTM Standard Method 3328-78; such comparison is greatly aided by overlaying sample and standard chromatograms utilizing a computer data system. The analyst must be familiar with the chromatography of a wide variety of products and must have established a library of reference chromatograms on the analytical system used. The standard most nearly matching the sample chromatogram(s) is selected and used for response calibration.

7.2.1.1 Provision of an uncontaminated sample suspected to be the source of an environmental incident can be very helpful in this identification process.

7.2.1.2 Petroleum products are complex mixtures of compounds derived from crude petroleum which are subject to degradation in the environment at varying rates with consequent changes in chromatographic profile. Artificial degradation of a standard material by partial evaporation or other techniques may be helpful in identifying degraded products.

7.2.2 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with methylene chloride. One of the external standards should be at a concentration near, but above, the quantitation limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.3 Using injections of 1 to 5 μL of each calibration standard, tabulate area responses against the mass injected. The results can be used to prepare a calibration curve for each mixture. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (<20% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

$$\text{CF} = \text{As}/\text{Cs}$$

where: As = Area of the Standard
 Cs = Concentration of the Standard

7.2.4 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than +/- 20%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Grab samples must be collected in glass containers (one-liter jars are recommended) with Teflon lined lids. Conventional sampling practices should be followed. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

8.2 The samples must be iced or refrigerated at $<6^{\circ}\text{C}$ from the time of collection until extraction.

8.3 Water samples must be extracted within 7 days of collection, soil samples must be extracted within 14 days of collection and all sample extracts must be analyzed within 40 days of extraction.

9.0 PROCEDURE

9.1 Extraction

9.1.1 Refer to Chapter Two of the USEPA SW-846 Methods, third Edition, for guidance on choosing the appropriate extraction procedure. The following paragraphs in this section summarize the methods for aqueous samples, for soils and other solids, and for organic wastes. The SW-846 methods referenced must be referred to for specifics on procedures, quality control, and other aspects.

9.1.2 In general, water samples are extracted at unmodified pH with methylene chloride or 1,1,2-trichloro-1,2,2-trifluoroethane. Either Method 3510 or 3520 may be used. To achieve maximum

sensitivity with this method, the extract should be concentrated to 1-mL or less if concentrations of analytes or other extractable materials in the sample permit.

9.1.3 Solid samples are extracted with methylene chloride or 1,1,2-trichloro-1,2,2-trifluoroethane using either Method 3540 or 3550. To achieve maximum sensitivity with this method, the extract should be concentrated to 1-mL or less if concentrations of analytes or other extractable materials in the sample permit.

Note: Changes in technology may allow for use of alternate extraction procedures to be used by labs in preparing samples for analysis. Approval of these alternate procedures must be obtained from the Iowa DNR Laboratory Certification Program prior to their implementation. Data from a series of four mid range spikes in the appropriate matrix as in Section 11.2 and a Method Detection Limit/Quantitation Limit study showing equivalency to the Quantitation Limits in Table 1 should be submitted.

9.1.4 Highly contaminated soils or solids or samples where lowest quantitation limits are not required may be extracted using smaller sample size or less concentration of the extract.

9.1.5 Organic wastes soluble in the extraction solvent (methylene chloride or trichlorotrifluoroethane) may be diluted with solvent in accord with method 3580 and analyzed.

9.2 Gas Chromatographic Analysis

9.2.1 Table 1 lists some of the petroleum derived products that may be analyzed by this procedure. Additional products and individual organic compounds may be analyzed by the method also, but application of the method must be demonstrated by analysis of spiked media.

9.2.2 Suggested gas chromatographic conditions are as follows:

Injection mode: Splitless, splitter turned on at first appearance of solvent front.

Splitter Sweep: 200 mL/min He.

He: 30 psi

Air: 300 psi

Hydrogen: 30 psi

Linear Velocity: 20 cm/sec.

Temperatures: Injector 300 °C, Detector 300 °C, Oven 50 ° C for 4 min then 10 °C/min to 320 °C, hold for 30 min.

9.2.3 Inject 1 to 5 µL of the sample in methylene chloride using the solvent flush technique or an autosampler.

9.2.4 Because the petroleum products are complex mixtures, definition of a retention time window and automated quantitative analysis with a chromatographic data system may not be readily feasible.

9.2.5 If the chromatographic response for the analyte exceeds the working range of standards, dilute the extract and reanalyze.

10.0 CALCULATIONS

10.1 Determine the concentration of the analyte in the sample.

10.1.1 Using the external standard method, calculate the amount of material injected from the chromatographic response. The concentration can be calculated from the equation:

$$\text{Concentration (mg/L)} = \frac{(A)(Vt)}{(CF_{\text{avg}})(Vs)}$$

A = Total Area of peaks in Retention Time

Window for Specific Product

CF_{avg} = Average Calibration Factor

Vt = volume of total (final) extract (μL)

Vs = volume of water extracted (mL)

Product Retention Time Window = Time when product first elutes/rises from baseline to the time when product elution returns to the baseline

Concentrations in mg/kg can be calculated by substituting for Vs the weight of the sample (solid) in grams.

As most of these analytes/products are mixtures containing more than one peak, the concentration of the samples are obtained by totaling the concentrations determined using the area of all peaks.

Note: Integration of petroleum products - The petroleum products that are the primary concern under the State of Iowa's Underground Storage Tank Program consist of a large number of different hydrocarbon components which may not be fully resolved chromatographically. Undegraded diesel fuel, fuel oil and kerosene show large, easily-resolved peaks due to selected components like the normal alkanes and a few isoprenoids, but the chromatographic profile consists of an underlying background of unresolved components which are part of the material. Generally, degraded products have reduced isolated peaks relative to the unresolved portion. The chromatographic profile of motor oil, another common pollutant, consists primarily of a broad "hump" of unresolved components. It is likely that heavier compounds like naphthalene and benzo(a)pyrene, of importance from a health effects standpoint, are part of the unresolved background. This unresolved background is, in fact, part of the material and for accurate quantitation **must** be included in the integration. It is important that proper integration including the unresolved components be performed by all laboratories since the integrated response may be used as a surrogate for estimation of the concentrations of the target compounds under RBCA.

10.1.2 Sample concentrations should be reported in relation to the commercial product(s) that was used as a calibration standard for the result. If the pattern of the sample does not match the

chromatographic pattern of the standard(s) a statement should be made on the report indicating that the patterns do not match. Chromatograms should be available upon request to illustrate the match obtained. Examples of Terminology that may be used for this reporting are TEH-Diesel, TEH-Gasoline, TEH-Motor Oil, etc. Due to possible mixing of products in samples it may be necessary to report more than one TEH-“Product” result for each sample.

10.1.3 Report results in mg/L for liquids or mg/kg for solids or organic liquids. The results are not corrected for recovery data.

Note: Products used as standards in this method may have retention time windows that overlap (share) portions of their retention time windows with other hydrocarbon containing products used as standards in this procedure. Caution should be exercised when evaluating results to assure that reviewers are aware that this shared area may be used in the quantitation of similar products.

11.0 QUALITY CONTROL

11.1 The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of blanks and quality control spikes as continuing checks on performance.

11.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 11.2.

11.1.2 The laboratory must prepare and analyze a quality control spike with each set of samples extracted (at least one spike for every 20 samples) to monitor continuing laboratory performance. The material selected and amount spiked should be appropriate for the samples being analyzed.

11.1.3 The laboratory should maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within accuracy and precision limits expected of the method.

11.1.4 In recognition of the rapid advances that are occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements which do not compromise quantitation or qualification of the results of the method. Each time such modifications are made to the method, the analyst is required to repeat the procedure in Section 11.2.

11.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

11.2.1 Select a representative spike concentration for each compound or mixture to be measured. Using stock standards, prepare a quality control check sample concentrate in appropriate solvent (acetone) 1000 times more concentrated than the selected concentrations.

11.2.2 Using a pipet, add 1.00 mL of the check sample concentrate to each of a minimum of four 1000-mL aliquots of reagent water. Analyze the aliquots according to the method beginning in Section 9.

11.2.3 Calculate the average percent recovery, (R), and the standard deviation of the percent recovery (s), for the results.

11.2.4 Note the average recovery (X) and standard deviation (p) found for each method parameter.

11.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and parameter being measured.

11.3.1 Calculate upper and lower control limits for method performance:

Upper Control Limit (UCL) = $R + 3s$

Lower Control Limit (LCL) = $R - 3s$

where R and s are calculated as in Section 11.2.3.

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance. Spike recovery data obtained with each set of samples must be compared with these limits and corrective action taken if recovery is outside the limits. Corrective action should consist of the following sequence:

- Check to be sure there are no errors in calculations or standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

11.4 Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against laboratory contamination. The analyst should also demonstrate through the analysis of a one-liter aliquot of reagent water or a blank solid matrix, that all glassware and reagent interferences are under control at any time there is suspected carryover or contamination.

12.1 REFERENCES

1. United States Environmental Protection Agency, "SW-846 Test Methods for Evaluating Solid Waste", 3rd Ed., Chapters One, Two, and Four and Methods 3500, 3510, 3520, 3540, 3550, 8000, and 8100.
2. American Society for Testing and Materials, "Standard Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography", ASTM 3328-78 (Reapproved 1982).
3. University Hygienic Laboratory, Iowa City, Iowa, Method OA-2, previous revisions 1/15/15, 7/1/91, 1/10/90.

Table 1. Single Laboratory Quantitation Limits

Type of Petroleum Product	Quantitation Limit	
	Water	Soil
Mineral spirits	0.1 mg/L	3 mg/kg
Kerosene	0.1 mg/L	3 mg/kg
Diesel fuel	0.1 mg/L	3 mg/kg
Fuel oil	0.1 mg/L	3 mg/kg
Motor oil	0.1 mg/L	3 mg/kg
Hydraulic fluid	0.1 mg/L	3 mg/kg