**Methods used by the Emergencies Science and Technology Section (ESTS) of Environment and Climate Change Canada, for the analysis of the physiochemistry, fate, and behaviour of petroleum products**

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**Preparation of the weathered fraction (12.01/x.x/M)**

An oil-weathering technique by rotary evaporation is used by the Emergencies Science and Technology Section (ESTS) to artificially weather oils through varying degrees of weight loss. The oil-weathering system consists of a Buchi R220 rotary evaporator with a 10 L flask, an integral water bath, a circulating bath, and a vacuum pump (Buchi Labortechnik AG, Flawil, Switzerland). The water bath, in contact with the rotary flask, is kept at 80 °C. The rotation speed is set to 135 rpm. The following procedure is used to evaporate oils:

* The water bath is brought to a temperature of 80 °C;
* The empty rotary flask is weighed, approximately 2 L of oil is added, and the flask is reweighed;
* The flask is mounted onto the water bath and the flask partially immersed in the water bath and spun at 135 rpm. A constant flow of air of 13 L/min through the flask is maintained by the vacuum pump;
* At set intervals, the sample flask is removed and weighed. Periodically, approximately 1 g of sample is reserved for chemical analysis.

Typically, three weathered fractions are prepared for each oil sample. The initial weathering period is 48 h, a duration chosen to simulate a heavily-weathered state of an oil in the environment. In addition, intermediate fractions are prepared having approximately one- and two-thirds of the total 48-h mass-loss. The exact time taken to prepare these intermediate fractions is determined by an estimation from the measured fractional mass-loss as a function of time for the 48-h sample. The fraction mass-loss is calculated as:

*%weathering* = (*mi* - *mf*) / (*mi* - *me*) × 100% (1)

where

*%weathering* is the percentage evaporative mass-loss over the 48-h period,

*mi* is the initial mass of the flask and oil,

*mf* is the final mass of the flask and oil,

*me* is the mass of the empty flask.

*Ref: Fieldhouse, B., B.P. Hollebone, N.R. Singh, T.S. Tong, and J. Mullin. 2010. “Artificial weathering of oils by rotary evaporator”, in the Proceedings of the 33rd AMOP Technical Seminar on Environmental Contamination and Response, Environment Canada, Ottawa, ON, 1:159–180,*

**Physical methods**

**Density (ASTM D5002)**

The density of the oil samples, in g/mL, is measured using an Anton Paar DMA 5000 or an Anton Paar Stabinger Viscometer SVM 3000 (Anton Paar, Montreal PQ, Canada). Measurements are made for a range of temperatures to simulate possible spill conditions. Method and operator performance are monitored by periodic measurements of a viscosity & density reference standard from Anton Paar and CONOSTAN*.* The mean of three replicates are reported for sample density. The API gravity at 60 °F (15.56 °C) is calculated by extrapolation from the density/temperature curve based on following equations.

*API Gravity = [141.5/ (specific gravity at 15.6 °C) - 131.5] (2)*

*Specific gravity at 15.6 °C = ρ0 exp [( ln ρ15 - ln ρ0 )/15 × 15.56 ] / ρ (H2O)15.56  (3)*

where ρ0 and ρ15 are the measured oil densities at 0 °C and 15 °C, respectively, and ρ (H2O)15.56 is the literature value for the density of water at 15.56 °C.

**Dynamic viscosity (ASTM D7042, 12.05/1.0/M, 12.06/X.X/M, 12.05/2.0/M, and 12.05/3.0/M)**

The dynamic viscosities of the samples, in mPa (cP), are measured using different methods and instruments depending on the type and viscosity range of the sample. A HAAKE RotoVisco 20 Viscometer (Thermo Fisher Scientific, Waltham, MA) with a rotor-cup geometry was used for the analysis of light, medium, and high viscosity oils (12.05/1.0/M). A HAAKE RS300 and then later RS6000 Rheometer with plate-plate geometry were used for the analysis of oils having a medium, high, and very high viscosity (12.06/X.X/M). A HAAKE VT550 Viscometer (Thermo Fisher Scientific, Waltham, MA) with a rotor-cup geometry is used for the analysis of light, medium, and high viscosity oils (12.05/2.0/M). An Anton Paar Stabinger SVM 3000 Viscometer (Anton Paar, Montreal PQ, Canada) is used for the analysis of light and medium viscosity oils (ASTM D7042). Recently, a new HAAKE VTiQ Viscotester (Thermo Fisher Scientific, Waltham, MA), having both rotor-cup and plate-plate geometries, has been used for the analysis of light, medium, high, and very high viscosity oils (12.05/3.0/M). Instrument calibration is verified using a viscosity reference standard from the Cannon Instrument Company (State College, PA)*.* Measurements are performed at a range of temperatures to simulate possible spill conditions. The mean of three replicates are reported for sample viscosity.

**Interfacial and surface tension (Modified ASTM D971 and 12.12/X.X/M)**

*Modified ASTM D971:*

This is the older method that is used at ESTS for measuring interfacial tension. The interfacial tensions of oil-air, oil-water, and oil-33 ‰ brine (3.3 % w/w NaCl in distilled, deionized water) are measured using a Krüss K10 Tensiometer following the Du Noüy ring method at 0 °C and 15 °C. The force required to pull a small platinum ring through the interface is measured by an analytical balance. Corrections are made to account for the amount of liquid lifted by the ring. Using the known size of the ring, the energy per unit area of the interface is calculated using at least three replicates.

*12.12/X.X/M:*

The surface and interfacial tensions are determined by a pendant drop technique using a CAM 200 contact angle and surface tension meter (KSV Instruments, Helsinki, Finland). Both oil-freshwater (distilled, deionized) and oil-brine (33 ‰), interfacial tensions are measured by forming an oil drop in the water phase. A J-hook needle is used to form a rising drop of oil sample in the denser water. The surface tension between oil and air is determined by forming a hanging oil drop in air.

Images are recorded for 10 s at a rate of 12 frames per second (FPS) (10 s × 12 FPS = 120 frames). The images are analyzed with a drop profile fitting method. Then, three replicates are averaged to determine the interfacial tension (mN/m).

**Water content (ASTM E203)**

The mass of water in an emulsion, expressed as a percentage by mass, is determined by Karl Fischer titration using a Metrohm 901 automatic titrator. The method closely follows ASTM E203 for volumetric titration. A 1:1:2 (by volume) mixture of methanol: chloroform: toluene is used as a working fluid. The auto-titrator is loaded with 5 mg/mL, pyridine-free Karl Fischer reagent from a certified supplier. Samples are replicated three times and the mean is reported as the water percentage. Calibration of the instrument is checked by a series of five replicate titrations of 25 µL of distilled, deionized water.

**Pour point (ASTM D97 and D5949)**

Pour point analysis is performed following ASTM D97 and ASTM D5949. At present, a Phase Technology 70Xi Pour Point Analyzer is used for the automated pour point analysis, where a 150 µL of sample is used for measurements at temperature intervals of 3 ºC. The mean of three replicates is reported as the sample pour point.

**Flash point (ASTM D7094, D56, and D93/IP34)**

Flash point analysis follows ASTM D7094 using a fully automated Grabner MiniFlash FLP or FLPL Analyzer. A 2-mL sample, placed in a 7-mL test cup containing a stirring magnet, is used for this analysis. When the small volume sample limits flash point detection, either ASTM D56 or D93/IP34 can be used as alternatives using outsourced instruments. The mean of three replicates is reported as the sample flash point.

**Sulphur content (ASTM D4294)**

Sulphur content is determined using Energy Dispersive X-ray Fluorescence Spectroscopy (ARL Quant’X EDXRF Spectrometer, Thermo Scientific) following ASTM D4294. The mean of three replicates is reported as the sample sulphur content.

**Adhesion (12.14/X.X/M)**

Oil adhesion is measured as the mass of oil per unit area that will remain on a standard test surface after ‘dipping and draining’ for 30 min.

An analytical pan scale having a precision of 0.0001 g is used with the provision for weighing from below the pan. In addition, a standard penetrometer needle adapted for hanging below the scale is required. The adhesion test is performed via the following procedure:

The scale is prepared by hanging a penetrometer needle, for which the surface area of the stainless steel has been calculated, from the balance hook and allowing for all to stabilize. The weight of the clean needle is zeroed. Approximately 80 mL of sample is poured into a 100-mL beaker. The beaker is elevated, using a lab jack, until the top of the stainless steel needle just touches the top of the oil surface. Care must be taken to avoid having the oil creep up onto the brass section of the needle, as the surface area calculation is based only on the stainless steel portion. The needle is left in the oil for 30 s, and then the beaker is lowered, allowing the needle to hang undisturbed. After 30 min, the mass of the oil on the needle is recorded. The oil adhesion is calculated as the average mass of oil remaining on the needle divided by needle’s surface area based on the mean value of three replicates.

**Evaporation equation (13.01/X.X/M)**

Evaporation kinetics, reported as percentage mass-loss (%Ev) as a function of time, are determined by measuring the mass-loss over time from a shallow dish. Approximately 20 g of oil is weighed into a 139 mm diameter petri dish. Measurements are conducted in a low-flow climate-controlled chamber at 15 °C. Temperatures are monitored by a digital thermometer. The oil mass is recorded at intervals using an electronic scale accurate to 0.01 g and collected on a computer logging system. The evaporation period can last from a few days for light oils to weeks for heavier products. The time versus mass-loss data series is fitted to either a

square-root or a natural logarithm function with the simplest and most representative equation being retained. The best-fit equations have the form:

*%Ev* = (A + B (*T*-15)) ln *t* (3)

*%Ev* = (A + B (*T*-15)) *t*1/2 (4)

where:

*%Ev* is the quantity of oil evaporated, as a percentage of the starting oil mass,

*T* is the oil surface temperature (°C),

*t* is time (in min),

A and B are constants fit to the measured data.

The relationship for the *A* and *B* constants is defined by Fingas (2004). The apparatus is periodically checked by conducting a run with a 15-g mass in place of the oil.

*Ref: Fingas, M.F. 2004. “Modeling evaporation using models that are not boundary-layer regulated”, Journal of Hazardous Materials, 107 (1–2): 27–36.*

Oil/brine emulsion formation tendency and stability (13.02/X.X/M)

Water-in-oil emulsions are formed in 2.2-L fluorinated vessels on an end-over-end rotary mixer (Associated Design, VA) at a nominal rotational speed of 50 RPM. Samples are prepared as follows:

* 600 mL of salt water (3.3 % w/v NaCl) is dispensed into a mixing vessel.
* A 30-mL aliquot of oil is added to each vessel to produce a 1:20 oil:water ratio.
* 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 room at 15 °C.
* The vessels and their contents then stand for approximately 4 h prior to rotation, then are mixed continuously for 12 h.
* After mixing, the emulsions are immediately collected from the vessels and measured for water content, viscosity, and the *complex modulus.* The emulsions are stored for one week in a cold room at 15 °C and changes in physical appearance are monitored.

Emulsions are classified into one of four stability classes: unstable, entrained water, meso-stable, and stable.

The *complex modulus* is measured using an RS300 RheoStress rheometer having a 35-mm plate-plate geometry. A stress sweep is performed over a 0.1 to 10 mPa range in a forced oscillation mode at a frequency of 1 Hz. The *complex modulus* value in the linear viscoelastic region is reported. Three replicate emulsions are prepared and the water content and *complex modulus* analyses are performed in duplicate for each emulsion sample.

*Ref: Fingas, M.F., B. Fieldhouse, 2004. “Formation of water-in-oil emulsions and application to oil spill modelling.” Journal of Hazardous Materials, 107:37–50.*

**Chemical dispersibility (ASTM F2059)**

Chemical dispersibility is assessed as a relative ranking of effectiveness for the dispersibility of an oil sample by the surfactant Corexit 9500 A. This method closely follows ASTM F2059. The mean of three replicates is reported as the sample chemical dispersibility.

**Chemistry methods**

**Simulated distillation (5.10/X.X/M, ASTM D2887*,* ASTM D7169,and the combined methods ofASTM D6730 and D7169)**

Simulated distillation curves were measured according to 5.10/X.X/M, ASTM 2887, ASTM D7169, and a combination of ASTM D6730 and D7169, depending on sample type and the availability of the instruments.

*SIMDIS (5.10/X.X/M):*

This analysis is performed using a gas chromatograph SIMDIS analyzer. The system has a custom cryogenically-cooled inlet and a high-temperature column. Reference and calibration mixtures are run according to instrument specifications.

Oil samples are made up as 2 % (m/m) solutions in carbon disulfide. An aliquot of 0.5 µL is

injected into the inlet. The inlet temperature runs from 40 to 430 °C, increasing at 70 °C/min. The oven temperature runs at -20 °C for 1 min, then increases at 10 °C/min to 430 °C, then maintains this final temperature for three minutes. The flame ionization detector operates at 430 °C. The instrumental software outputs a series of simulated boiling point ranges as a function of temperature.

**Fractional analysis of hydrocarbon groups (12.11/4.0/M, 12.11/3.0/M, 12.11/1.0/M, 12.11/4.0/M, 12.11/2.0/M)**

*Asphaltene and resin fractional analysis (12.11/1.0/M):*

Asphaltenes are precipitated from the original oil by using excess *n*-pentane as the precipitating medium (12 mL *n*-pentane/g of oil). The beaker is stirred vigorously with a glass rod then warmed in a warm water bath for 10 s with intermittent swirling. Next, the mixture is filtered through a pre-weighed 0.45 µm pore filter. The filter residue (asphaltenes) is rinsed with *n*-pentane and then transferred with the filter to a weighing boat and dried in a desiccator. The mass is measured to calculate the asphaltene content.

The filtrate fluid (the maltenes) is rotary-evaporated at low pressure to remove the solvent, and then quantitatively transferred into a 100-mL volumetric flask and diluted up to the 100-mL mark using *n*-pentane. Activated silica gel (15 g) is packed into a column and topped off with 1.5 cm of anhydrous Na2SO4. A 5.0-mL aliquot of diluted maltene is then pipetted into the column. A 60-mL mixture of 1:1 benzene/hexane is used to elute the saturates and aromatics. Resins are then eluted using 60 mL of methanol, followed by 60 mL of dichloromethane, and collected in a 500-mL boiling flask. The collected resin portion is rotary-evaporated and then quantitatively transferred to a pre-weighed amber vial. The content in the vial is completely dried using nitrogen. Resin content is calculated by measuring the mass, then applying the dilution factor. The mean of three replicates is reported for analysis of asphaltene and resin fractions.

*Asphaltene and resin fractional analysis (12.11/3.0/M):*

Asphaltenes are precipitated from the original oil by using excess *n*-pentane as the precipitating medium (30 mL *n*-pentane/g of oil). The flask is placed on an incubator shaker for horizontal plane rotary mixing at 100 RPM for 1 h at 20 ºC. Next, the mixture is filtered through a pre-weighed 0.45 µm pore filter. The filter residue (asphaltenes) is rinsed with *n*-pentane and then transferred with the filter to a weighing boat and dried in a desiccator. The mass is then measured to calculate the asphaltene content.

The filtrate fluid (the maltenes) is rotary-evaporated at low pressure to remove the solvent, and then quantitatively transferred into a 100-mL volumetric flask and diluted up to the 100-mL mark using *n*-pentane. Activated silica gel (30 g) is packed into a column and topped off with 1.5 cm of anhydrous Na2SO4. A 5.0-mL aliquot of diluted maltene is then pipetted into the column. A 180-mL mixture of 1:1 benzene/hexane is used to elute the saturates and aromatics. Resins are then eluted using 100 mL of methanol, followed by 100 mL of dichloromethane, and collected in a 500-mL boiling flask. The collected resin portion is rotary-evaporated and then quantitatively transferred to a pre-weighed amber vial. The content in the vial is completely dried using nitrogen. Resin content is calculated by measuring the mass, then applying the dilution factor. The mean of three replicates is reported for analysis of asphaltene and resin fractions.

*Asphaltene and resin fractional analysis (12.11/4.0/M):*

Asphaltenes are precipitated from the original oil by using excess *n*-pentane as the precipitating medium (30 mL *n*-pentane/g of oil). The flask is placed on an incubator shaker for horizontal plane rotary mixing at 100 RPM for 1 h at 20 ºC. Next, the mixture is filtered through a pre-weighed 0.45 µm pore filter. The filter residue (asphaltenes) is rinsed with *n*-pentane and then transferred with the filter to a weighing boat and dried in a desiccator. The mass is then measured to calculate the asphaltene content.

The filtrate fluid (the maltenes) is rotary-evaporated at low pressure to remove the solvent, and then quantitatively transferred into a 100-mL volumetric flask and diluted up to the 100-mL mark using *n*-pentane. Activated silica gel (30 g) is packed into a column and topped off with 1.5 cm of anhydrous Na2SO4. A 10.0-mL aliquot of diluted maltene is then pipetted into the column. A 180-mL mixture of 1:1 benzene/hexane is used to elute the saturates and aromatics. Resins are then eluted using 100 mL of methanol, followed by 100 mL of dichloromethane, and collected in a 500-mL boiling flask. The collected resin portion is rotary-evaporated and then quantitatively transferred to a pre-weighed amber vial. The content in the vial is completely dried using nitrogen. Resin content is calculated by measuring the mass, then applying the dilution factor. The mean of three replicates is reported for analysis of asphaltene and resin fractions.

*Wax content (12.11/2.0/M):*

Waxes are separated by crystallization in polar solvent. The remaining diluted maltene after resin quantification (95.0 mL) is rotary-evaporated to remove the solvent and quantitatively transferred into a 250-mL Teflon Erlenmeyer flask, using 50 mL of 1:1 (v:v) dichloromethane (DCM)/Methyl Ethyl Ketone (MEK). The Teflon flask, Buchner funnel, 125-mL filtering flask, and a squeeze bottle of 1:1 DCM/MEK are placed in the -30 °C freezer to chill overnight and to crystallize the wax. The contents of the Teflon flask are filtered. The wax fraction retained on the filter is dried in the desiccator until a constant mass is achieved. The mass of the recovered waxes is recorded to calculate the wax content (correction factor = 100/90, where 100 is the initial diluted volume (mL) of maltene, and 95 is the volume (mL) of maltene used for the wax content analysis). The mean of three replicates is reported for the analysis of wax content.

*Wax content (12.11/4.0/M):*

Waxes are separated by crystallization in polar solvent. The remaining diluted maltene after resin quantification (95.0 mL) is rotary-evaporated to remove the solvent and quantitatively transferred into a 250-mL Teflon Erlenmeyer flask, using 50 mL of 1:1 (v:v) dichloromethane (DCM)/Methyl Ethyl Ketone (MEK). The Teflon flask, Buchner funnel, 125-mL filtering flask, and a squeeze bottle of 1:1 DCM/MEK are placed in the -30 °C freezer to chill overnight and to crystallize the wax. The contents of the Teflon flask are filtered. The wax fraction retained on the filter is dried in the desiccator until a constant mass is achieved. The mass of the recovered waxes is recorded to calculate the wax content (correction factor = 100/95, where 100 is the initial diluted volume (mL) of maltene, and 90 is the volume (mL) of maltene used for the wax content analysis). The mean of three replicates is reported for the analysis of wax content.

*Calculation of Saturates and Aromatics by difference:*

The final percentages of saturates and aromatics are calculated by the deduction of percentage asphaltene and resin from the 100 % of original oil. Saturate and aromatic fractions are estimated using the amounts of GC-detectable total saturate hydrocarbon (TSH) and GC-detectable total aromatics hydrocarbon (TAH) relative to the GC-detectable total petroleum hydrocarbons (TPH) (i.e., %TAH/TPH and %TAS/TPH), respectively.

**Semi-volatile components in oil and environmental samples (5.03/X.X/M)**

*Sample preparation:*

Prior to use, all clean glassware is rinsed with acetone, DCM, and then hexane. The solvent blank is combined and analyzed by GC-FID and GC-MS. The results must demonstrate that the glassware is clean and target-analyte free.

The oil samples are transferred and dissolved in hexane for further column cleanup. A sample containing 16 to 20 mg of total oil is quantitatively transferred into a 3-gram silica gel chromatography column for sample cleanup and fractionation. Hexane (12 mL) and 50 % DCM in hexane (v/v, 15 mL) are used to elute the saturated and aromatic hydrocarbon fractions, respectively. These fractions are concentrated under gentle streams of nitrogen, spiked with appropriate internal standards (IS) (including 5-α-androstane, C30 ββ-hopane, and [*2H*14] terphenyl for GC-detected petroleum hydrocarbons (GC-TPH) and *n*-alkanes, biomarkers, and PAHs analysis, respectively), and then adjusted to 1.0 mL for GC-MS and GC-FID analyses.

For each sample, the hexane-eluted fraction (labelled as *F*sat) is used for analysis of aliphatic hydrocarbons, including total GC-detectable total saturated hydrocarbons (GC-TSH), alkanes, and biomarker of terpanes, saturated steranes. The 50 % DCM fraction (labelled as *F*arom) is used for the analysis of total GC-detectable total aromatic hydrocarbons (GC-TAH), alkylated PAHs, and other unsubstituted PAHs. Equal portions of *F*sat and *F*arom are combined (labelled as the combined fraction) and used for determining the GC-TPH (including the unresolved complex mixture of hydrocarbons (UCM)). The recovery for all the surrogates in the studied samples, reference oil (13.1 % weathered Prudhoe Bay crude oil), and blank controls are evaluated for quality control and quality assurance.

*Instruments and sample analysis:*

The GC-TPH (~*n*-C8 through *n*-C50) is determined by GC-FID using a DB-5HT fused-silica column (30 m × 0.25 mm i.d., 0.10 μm film thickness). Target *n*-alkanes (~*n*-C9 to *n*-C40), PAHs, and biomarker compounds are analyzed by GC-MS using a DB-5 MS capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness) in the selective ion monitoring mode. The target alkanes, biomarkers of terpanes and steranes, and PAHs are shown in Table 1.

*Ref: Yang, C., Z.D. Wang, B. Hollebone, C.E. Brown, Z.Y. Yang, and M. Landriault. 2015. “Chromatographic fingerprinting analysis of crude oil and petroleum products” In: M. Fingas, Ed.;* Handbook of Oil Spill Science and Technology*; John Wiley & Sons, Inc.; pp. 95–163.*

**Table 1. Target list for semi-volatile chemical analysis in oil and environmental samples**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **n-Alkanes** | **Biomarker compounds** | | **Alkylated PAHs** | |
| *n*-*C*9 | C21 tricyclic terpane | TR21 | C0-Naphthalene | C0-N |
| *n*-*C*10 | C22 tricyclic terpane | TR22 | C1-Naphthalenes | C1-N |
| *n*-*C*11 | C23 tricyclic terpane | TR23 | C2-Naphthalenes | C2-N |
| *n*-*C*12 | C24 tricyclic terpane | TR24 | C3-Naphthalenes | C3-N |
| *n*-*C*13 | 18α (H),21β(H)-22,29,30-trinorhopane | Ts | C4-Naphthalenes | C4-N |
| 2,6,10-trimethyldodecane | 17 α (H),21 β (H)-22,29,30-trinorhopane | Tm | C0-Phenanthrene/anthracene | C0-P |
| *n*-*C*14 | 17 α (H),21 β (H)-30-norhopane (H29) | H29 | C1-Phenanthrenes/anthracenes | C1-P |
| *n*-*C*15 | 17 α (H),21 β (H)-hopane | H30 | C2-Phenanthrenes/anthracenes | C2-P |
| n-C16 | 22*S*-17 α (H),21 β (H)-30-homohopane | H31S | C3-Phenanthrenes/anthracenes | C3-P |
| 2,6,10-trimethylpentadecane | 22*R*-17 α (H),21 β (H)-30-homohopane | H31R | C4-Phenanthrenes/anthracenes | C4-P |
| *n*-C17 | 22*S*-17 α (H),21 β (H)-30,31-bishomohopane | H32S | C0-Dibenzothiophene | C0-D |
| Pristane | 22*R*-17 α (H),21 β (H)-30,31-bishomohopane | H32R | C1-Dibenzothiophenes | C1-D |
| *n*-C18 | 22*S*-17 α (H),21 β (H)-30,31,32-trishomohopane | H33S | C2-Dibenzothiophenes | C2-D |
| Phytane | 22*R*-17 α (H),21 β (H)-30,31,32-trishomohopane | H33R | C3-Dibenzothiophenes | C3-D |
| *n*-C19 | 22*S*-17 α (H),21 β (H)-30,31,32,33-tetrakishomohopane | H34S | C0-Fluorene | C0-F |
| *n*-C20 | 22*R*-17 α (H),21 β (H)-30,31,32,33-tetrakishomohopane | H34R | C1-Fluorenes | C1-F |
| *n*-C21 | 22 S-17 α (H),21 β (H)-30,31,32,33,34-pentakishomohopane | H35S | C2-Fluorenes | C2-F |
| *n*-C22 | 22*R*-17 α (H),21 β (H)-30,31,32,33,34-pentakishomohopane | H35R | C3-Fluorenes | C3-F |
| *n*-C23 | C27 20-5 α (H),14 β (H),17 β (H)-cholestane | *C*27 α β β | C0-Fluroanthene/pyrene | C0-Fl |
| *n*-*C*24 | C28 20-5 α (H),14 β (H),17 β (H)-ergostane | *C*28 α β β | C1-Fluroanthenes/pyrenes | C1-Fl |
| *n*-*C*25 | C29 20-5 α (H),14 β (H),17 β (H)-stigmastane | *C*29 α β β | C2-Fluroanthenes/pyrenes | C2-Fl |
| *n*-*C*26 |  |  | C3-Fluroanthenes/pyrenes | C3-Fl |
| *n*-*C*27 |  |  | C4-Fluroanthenes/pyrenes | C4-Fl |
| *n*-*C*28 |  |  | C0-Benzonaphthothiophenes | C0-B |
| *n*-*C*29 |  |  | C1-Benzonaphthothiophenes | C1-B |
| *n*-*C*30 |  |  | C2-Benzonaphthothiophenes | C2-B |
| *n*-*C*31 |  |  | C3-Benzonaphthothiophenes | C3-B |
| *n*-*C*32 |  |  | C4-Benzonaphthothiophenes | C4-B |
| *n*-*C*33 |  |  | C0-Chrysene | C0-C |
| *n*-*C*34 |  |  | C1-Chrysenes | C1-C |
| *n*-*C*35 |  |  | C2-Chrysenes | C2-C |
| *n*-*C*36 |  |  | C3-Chrysenes | C3-C |
| *n*-*C*37 |  |  | **Other unsubstituted PAHs** |  |
| *n*-*C*38 |  |  | Biphenyl | Bph |
| *n*-*C*39 |  |  | Acenaphthylene | Acl |
| *n*-*C*40 |  |  | Acenaphthene | Ace |
|  |  |  | Anthracene | An |
|  |  |  | Fluoranthene | Fl |
|  |  |  | Pyrene | Py |
|  |  |  | Benz(a)anthracene | BaA |
|  |  |  | Benzo(b)fluoranthene | BbF |
|  |  |  | Benzo(k)fluoranthene | BkF |
|  |  |  | Benzo(e)pyrene | BeP |
|  |  |  | Benzo(a)pyrene | BaP |
|  |  |  | Perylene | Pe |
|  |  |  | Indeno(1,2,3-cd)pyrene | IP |
|  |  |  | Dibenzo(ah)anthracene | DA |
|  |  |  | Benzo(ghi)perylene | BgP |

**Determination of BTEX and alkylbenzenes in crude oil and refined products (5.02/X.X/M)**

The determination of BTEX (benzene, toluene, ethylbenzene, and *p*-, *m*-, and *o*-xylene isomers) and alkylbenzenes in crude oil and refined products is designed to be specific, without using a solvent evaporation and concentration step, which may result in the loss of BTEX compounds due to their low boiling points and very volatile nature. In this method, oil samples are directly weighed and dissolved in *n*-pentane to an approximate concentration of 20 mg/mL (~0.2 g of oil is dissolved in *n*-pentane and diluted to 10 mL with *n*-pentane). Then, 100 µL of oil solution is spiked with d10-ethylbenzene as an internal standard and diluted ten times with *n*-pentane. The analysis of BTEX and alkylbenzenes is performed on an Agilent 7890 A gas chromatograph equipped with a Model 5975C mass selective detector (MSD). A DB-5 MS or equivalent fused-silica column (30 m × 0.25 mm i.d., 0.25 μm film thickness) is used for chromatographic separation. PIANO (paraffins, isoparaffins, aromatics, naphthenes and olefins) components containing 38 alkylated (C0- to C6-) benzenes were used as standard to quantify the target compounds. Table 2 lists the select target compounds.

**Table 2. BTEX and target C3-C6 alkylbenzenes**

|  |  |  |
| --- | --- | --- |
| **Compounds** | **Formula** | **Molecular weight** |
| **BTEX group** |  |  |
| Benzene (B) | C6H6 | 78 |
| Toluene (T) | C7H8 | 92 |
| Ethylbenzene (E) | C8H10 | 106 |
| *m*-& *p*-Xylene (X) | C8H10 | 106 |
| *o*-Xylene (X) | C8H10 | 106 |
| **C3 alkylbenzenes** |  |  |
| Isopropylbenzene | C9H12 | 120 |
| Propylebenzene | C9H12 | 120 |
| 3-Ethyltoluene | C9H12 | 120 |
| 4-Ethyltoluene | C9H12 | 120 |
| 1,3,5-Trimethylbenzene | C9H12 | 120 |
| 2-Ethyltoluene | C9H12 | 120 |
| 1,2,4-Trimethylbenzene | C9H12 | 120 |
| 1,2,3-Trimethylbenzene | C9H12 | 120 |
| **Selected C4-C6 alkyl benzenes** |  |  |
| Isobutylbenzene | C10H14 | 134 |
| 1-Methyl-2-isopropylbenzene | C10H14 | 134 |
| 1,2-Dimethyl-4-ethylbenzene | C10H14 | 134 |
| Amylbenzene | C11H16 | 148 |
| *n*-Hexylbenzene | C12H18 | 162 |