

Analysis of Whole Oil, Saturated and Aromatic Hydrocarbons, and Bitumen Extracts by Gas Chromatography—Flame Ionization Detection

1. Introduction

- The U.S. Geological Survey Central Energy Resource Science Center (CERSC) uses this method to screen, correlate and characterize crude oil and extractable organic matter from source rocks (bitumen). Gas chromatograms of sample fluids are interpreted to derive characteristic parameters. The pristane to phytane ratio, four different carbon preference indices and three odd even predominance indices are calculated from the saturated hydrocarbon fraction, whole oil or bitumen gas chromatograms. These parameters can be used to gain a better understanding of the origin, maturity, and secondary alteration, of petroleum system components.

2. Interfaces with Other Methods

- Bitumen extract for this procedure is obtained from *EGL Method 03*
- Saturate and Aromatic Hydrocarbon fractions are obtained from *EGL Method 04*
- Method for Sample Login, Control, and Disposition (*EGL Method 25*)
- Detailed Procedure for the Operation of Instrumentation and Data processing for EGL Method 08 (*EGL Work Instruction 03, R0*)

3. Materials and Equipment

- Agilent¹ 6890 Gas Chromatograph with a Flame Ionization Detector (FID) and TotalChrom data acquisition software.
- Helium gas
- VWR FID gas station for purified air and hydrogen generation for FID
- Solvents (all high purity HPLC grade, optima or equivalent)
 - *Iso*-octane for saturates
 - Benzene for aromatics
 - Chloroform for bitumen
 - Carbon disulfide for whole oils
- Nitrogen evaporator; Organomation N-evap.
- 20-200 µL BrandTech® Transferpette® pipet
- 100-1000 µL BrandTech® Transferpette® pipet
- Disposable glass Pasteur pipet
- Syringe filters; 0.45 µm PTFE, non-sterile and
- Glass syringe with metal luer lock

¹ Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

4. Procedure

- Saturated and aromatic hydrocarbon fractions, and bitumen extracts are diluted or concentrated, if necessary, to bring the compounds of interest within the range of the FID. The sample is diluted when the chromatogram contains a response greater than 1000 mV excluding the solvent front. The sample is concentrated when the chromatogram contains small responses or when compounds of interest are not resolved. All gas chromatography (GC) analyses should be completed prior to drying the extracts for gravimetric determination (see **EGL Method 04**).
 - Acceptable chromatograms for saturated hydrocarbons can usually be obtained without dilution or concentration. If dilutions are needed; use iso-octane. A gentle stream of nitrogen gas provided by the nitrogen evaporator is used to concentrate the extract if the FID response is low.
 - Aromatic hydrocarbon fractions usually need to be concentrated to a volume of one to three mL using a gentle stream of nitrogen gas with a nitrogen evaporator. Benzene should be used for dilution of an aromatic fraction.
 - Bitumen extracts are taken directly from their volumetric flasks from EGL Method 03. All dilutions are made using chloroform or 1-2 mL of sample can be transferred using pipette from the volumetric flask to a 7 mL vial and concentrated using the nitrogen evaporator.
- Whole oil analysis is performed by dissolving a small amount of oil in carbon disulfide. Dilutions are made using carbon disulfide or sample is concentrated using a gentle stream of nitrogen gas with a nitrogen evaporator.
 - Place 500 μ L of carbon disulfide in a 7 mL vial. Transfer a small amount of oil by simply dipping the tip of a disposable glass pasteur pipet into the oil and then placing it into the 7 mL vial. The dissolved sample can then be diluted or concentrated as necessary.
- The Energy Geochemistry Laboratory has two gas chromatographs dedicated to this method. The whole oil and bitumen analyses are run on the instrument labeled AG6890 and the saturated and aromatic hydrocarbon analyses are run on the instrument labeled HP6890. (Both instruments are Agilent 6890 series.)
- Once all the compounds of interest have been resolved, the data is processed and imported into the laboratory information management system (LIMS). The LIMS is used to derive the pristane to phytane ratios, carbon preference index (CPI) and the odd-even predominance (OEP) from the peak areas and heights.
 - Details about the CPI and OEP used at the Central Energy Resource Science Center can be found in attached Carbon Preferential Index, P.G. Lillis.
- Comprehensive information on operating the gas chromatographs, data processing and compound lists can be found in the Detailed Procedure for the Operation of Instrumentation and Data Processing for EGL Method 08. (EGL Work Instruction 03).

5. Calibration and Quality Control Samples

- The in-house crude oil standard, Clifford Causey 04049_2 is used as a compound identification standard.
- 04049_2 crude is fractionated using EGL Method 04, R0 and the saturated and aromatic hydrocarbon fractions are used as compound identification standards.
- For a bitumen standard, 6-9 drops of 04049_2 crude is placed in a 7 mL vial and dissolved in approximately 7 mL of chloroform. This can be capped, and stored in a freezer and used for a compound identification standard as long as all compounds of interest are still present.
- Whole oil identification standard can be made following the same procedure described for bitumen above with carbon disulfide being used instead of chloroform.
- For whole oil and bitumen analyses a blank is run every five samples. For saturated and aromatic hydrocarbon analyses a blank is run every ten samples.
- Blanks used in each analytical run should use the same solvent that the extract or dissolved oil is analyzed in.
 - Saturates use iso-octane
 - Aromatics use benzene
 - Bitumen uses chloroform
 - Whole oil uses carbon disulfide

6. Limits, Precautions, and Interferences

- Concentrations of individual compounds are not determined using this method. Analytical limits have not been determined. Samples are run through the instrument and all dilutions or concentrations are performed in-order to resolve all possible compounds of interest for each particular sample.
- If chromatograms contain peak responses of greater than 1000 mV excluding the solvent front, a dilution is performed. If small responses are observed or no compounds of interest are observed during initial analysis, the sample is concentrated in order to resolve all possible compounds of interest.
- Whole oil and bitumen analyses are more prone to carry over and contamination because these samples contain the larger resin and asphaltene compounds. For this reason a blank is run every 5 samples and it is recommended to have one GC dedicated to running these analyses while other GC is used for the more “clean” saturated and aromatic fractions. The majority of the time, carryover and contamination of the whole oil and bitumen analyses can be eliminated by cleaning or replacing the injection needle, front inlet septum, liner, o-ring and gold seal, or cutting 1-2 feet off the front of the GC column.
- While performing whole oil analysis, it may be necessary to “cleanup” the starting crude oil material in order to prevent sediment or water from being introduced into the GC.
 - For water, the sample is centrifuged and a sample of oil is taken from the top of the oil layer

- If sediment or other floating material is observed in the oil, the sample can be centrifuged. If this does not separate the desired material, the sample can be filtered through a syringe filter (0.45 µm PTFE, non-sterile)

7. Acceptance of Data

- For all GC analyses, the in-house standard is run at the beginning of each job. . If all of the compounds of interest are not fully resolved or if peak shapes are abnormal, the job is stopped and the necessary maintenance or repairs to the instrument are performed by a trained analyst to resolve the problem.
 - All maintenance and repairs should be documented in the appropriate instrument logbook with the date, name or initials of analyst, what the problem was and how it was resolved.
- An instrument blank is run at the beginning and end of each job. For saturated and aromatic analyses, a blank is run every ten samples, while for whole oil and bitumen analyses, a blank is run every 5 samples.
 - If instrument blanks contain any measurable amounts of the compounds of interest or undesirable contamination, the analyst will take the necessary steps to eliminate any possible sample carryover or contamination. Any samples that were bracketed by the failed instrument blank are re-analyzed.

8. Data Handling and Transfer

- Raw files are processed and analyzed using TotalChrom to produce result files. Result files are converted to CDF files using TotalChrom. CDF files are submitted to the LIMS via a shared network folder and all ratios, CPI, and OEP calculations are performed by the LIMS.
 - Method, Report, Sequence and all raw files are stored under the appropriate instrument folder, year, LIMS job number, and type of analyses.(e.g. HP6890/2010/E101002/Saturates/*files*)
 - If samples are run more than once because a dilution or concentration was needed, another folder should be created under the appropriate analyses. (e.g. HP6890/E101002/Saturates/Run2/*files*)
 - Result files are processed and stored in the same folder that the acceptable raw file is stored in. For example, if an acceptable chromatogram was obtained on the first run than the result file for that raw file is stored in the location HP6890/2010/E101002/Saturates/*result file*. If an acceptable chromatograph is obtained on the second run after dilution or concentration the file is stored in HP6890/E101002/Saturates/Run2/*result file*.
 - Once a result file has been processed, it is converted into a .cdf (formally known as “AIA format”, the ANDI/netCDF scientific data exchange format) using the TotalChrom software.
 - The CDF is imported into the LIMS via a shared network folder. Once in the LIMS, results and calculations are validated by the analyst and

approved by an appropriate QA official before being released to the submitter.

- Calculations automated in the LIMS are displayed below.

Hunt 1979

$$CPI01 = \frac{1}{2} \left(\frac{C_{23} + C_{25} + C_{27} + C_{29} + C_{31}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} + \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} \right)$$

Bray and Evans 1961

$$CPI02 = \frac{1}{2} \left(\frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} + \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{26} + C_{28} + C_{30} + C_{32} + C_{34}} \right)$$

Philippi 1965

$$CPI03 = 2 \left(\frac{C_{29}}{C_{28} + C_{30}} \right)$$

Marzi and Others 1993

$$CPI04 = \frac{(C_{23} + C_{25} + C_{27}) + (C_{25} + C_{27} + C_{29})}{2 \times (C_{24} + C_{26} + C_{28})}$$

Scalan and Smith 1970 at n-C25, n-C27, and n-C29

$$OEP01 = \left(\frac{C_{23} + (6 \times C_{25}) + C_{27}}{(4 \times C_{24}) + (4 \times C_{26})} \right)^{-1^{24}}$$

$$OEP02 = \left(\frac{C_{25} + (6 \times C_{27}) + C_{29}}{(4 \times C_{26}) + (4 \times C_{28})} \right)^{-1^{26}}$$

$$OEP03 = \left(\frac{C_{27} + (6 \times C_{29}) + C_{31}}{(4 \times C_{28}) + (4 \times C_{30})} \right)^{-1^{28}}$$

Pristane and Phytane ratios

$$PRPH = \frac{\text{Pristane}}{\text{Phytane}}$$

$$PR17 = \frac{\text{Pristane}}{C_{17}}$$

$$PH18 = \frac{\textit{Phytane}}{C_{18}}$$

- For more detailed information on data processing see *Detailed Procedure for the Operation of Instrumentation and Data processing for EGL Method 08 (EGL Work Instruction 03)*
- For more detailed information on calculations performed by the LIMS see *Carbon Preferential Index, P.G. Lillis*.

9. References

- None

10. Attachments

- *Carbon Preferential Index, P.G. Lillis*

11. History of Changes

- R0: Initial Issue