Petroleum Geochemistry Research Laboratory Method for Determining Saturate, Aromatic, Resin, and Asphaltene Composition of Rock Extracts and Crude Oil

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Date Published: June 2020

Suggested Citation: Lowry, Z.K., 2020, Petroleum Geochemistry Research Laboratory (PGRL) Method for Determining Saturate, Aromatic, Resin, and Asphaltene Composition of Rock Extracts and Crude Oil: U.S. Geological Survey Web Page, available at https://doi.org/10.5066/P901N4FH

Keywords: SARA, Petroleum Geochemistry Research laboratory; PGRL; Saturate, Aromatic, Resin, Asphaltene

1. Method Summary

This method is used to gravimetrically determine the percent composition of saturate, aromatic, resin, and asphaltene compounds (SARA) of rock extracts or crude oil. In this method, rock extracts or extractable organic matter (EOM) may be referred to as bitumen. Bitumen is obtained from ground rocks by Soxhlet extraction with chloroform, and the concentration of bitumen, measured in parts per million (ppm), is determined gravimetrically. Asphaltenes are precipitated and separated from the bitumen or oil prior to performing liquid chromatography on the remaining mixture of saturates, aromatics, and resins, which are commonly referred to as maltenes. The SARA fractions are then dried and weighed to determine the percent composition. When determining the SARA composition of an oil, the percent volatile content of the oil (considered to comprise compounds with carbon numbers of ~15 and less; C_{15-}) is also measured and included in the total percent composition. The recovered fractions are also suitable for further characterization using techniques such as gas chromatography with flame ionization detection, isotope ratio mass spectrometry, or biomarker analyses by gas chromatography mass spectrometry.

2. Scope and Application

This method is used to determine the SARA composition of a wide variety of rock extracts and crude oils from natural systems or produced via laboratory processes (for example, extraction, centrifugation, or pyrolysis).

3. Interferences

3.1. Electrostatic charge around the glass vials and changes in ambient conditions may result in errors in weight measurements and may cause the weight measurements to drift over time. For this reason, steps should be taken to neutralize the static charge via a U-ionizer or similar technology, and it is suggested that the final weight and vial tare weight be measured on the same day or ideally within an hour of each other.

3.2. If water is present in the extract or if extracts are not filtered properly, calculated bitumen concentrations may not be representative of the true bitumen concentration. If a layer of water is observed in the final extract, sodium sulfate may be added to the extract to remove the water. Sodium sulfate is then removed during the filtration step.

3.3. To minimize exposure of the activated and partially deactivated silica and alumina to any moisture in the air, they must always be kept either in a desiccator, in a capped jar, or in a capped iso-octane slurry when not in use and during column preparation.

3.4. While packing the columns, air bubbles must not be allowed to form. The solvent level must not fall below the top of the alumina packing once the columns are made or while performing liquid column chromatography. Allowing air bubbles to form during assembly or allowing air channels to enter the column during chromatography, may cause poor separation.

3.5. To minimize vapor loss while measuring the initial weight of the oil for column chromatography, or for determining volatiles, these tasks must always be performed with a capped vial.

3.6. If water or sediment is present, or may be present in the sample, the oil can be centrifuged or passed through a 0.45 μm polytetrafluoroethylene (PTFE) syringe filter to remove the water or sediment prior to taking the initial weight of the oil.

3.7. Samples containing large amounts of wax or high resin content (for example, samples from the Green River Formation) are difficult to separate without coelution of the saturate, aromatic, and resin compound classes using one column. To mitigate this problem, one column is placed above another column, which effectively doubles the column length improving separation. When doing this, collection volumes during liquid chromatography are doubled, so additional collection vials or larger collection vials will be needed.

4. Safety Precautions

This method does not attempt to address health and safety concerns. Adherence to appropriate health, safety and regulatory practices are the responsibility of the end user.

5. Sample Handling, Preservation, Storage and Holding Times

There are no special sample handling procedures, containers (non-plastic is preferred), preservation conditions, or storage and holding times. Glass containers are recommended

for rock and oil samples. The amount of rock needed will depend on the richness of the rock being extracted. Organic-lean rocks might require more extraction material than organic-rich rocks (range is from approximately 0.1g to 150g). For oils it is recommended that a sample size of 200mg is used; 100mg for is needed for column chromatography and 100mg is needed for volatile determination. Less can be used if 200mg is not available.

6. Trademark Disclaimer

The use of trade, product, or firm names in this method is for descriptive purposes only and does not imply endorsement by the U.S. Government.

7. Apparatus and Reagents

7.1. Soxhlet Extraction

7.1.1. Glass wool: Pyrex brand or equivalent, baked at 425°C (±25°C) overnight.

7.1.2. 7mL clear glass vials with foil lined caps, baked at 425°C (±25°C) overnight.

7.1.3. Sheet of Copper cut into strips approximately 2.5inch by 0.75inches; JT Baker 99.9% pure or equivalent. Rinse thoroughly with chloroform.

7.1.4. Glass filter: Whatman grade GF/A glass microfiber, 55mm diameter or equivalent, baked at 425°C (±25°C) overnight.

7.1.5. Boiling Stones: Chemware™ brand, PTFE, or equivalent.

7.1.6. Soxhlet thimbles: Whatman high purity glass microfiber or equivalent. Internal diameter 43mm, external length 123mm, baked at 425°C (±25°C) overnight.

7.1.7. 500mL glass round-bottom flask.

7.1.8. Soxhlet apparatus: 55/50 top, 24/40 bottom, matching reflux condenser.

7.1.9. Heating mantle sized for 500mL round-bottom flask.

7.1.10. Mounting stand with clamps and hardware, variable transformer, plumbing, Neslab™ CT-33 refrigerated, recirculator or equivalent.

Figure 1. Soxhlet apparatus (7.1.6–7.1.10)

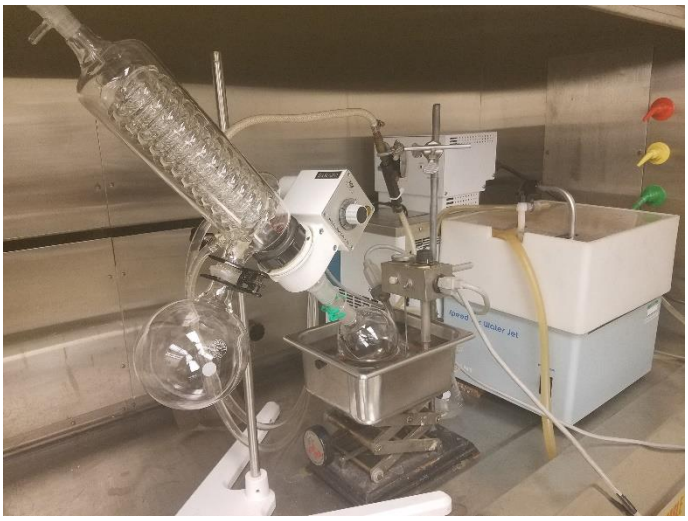
7.1.11. Long metal hemostatic clamp or tweezers approximately 12 inches long.

7.1.12. Funnel/filtration system consisting of: (1) fitted glass filter support base for 55mm filters with integral vacuum connector and 24/40 joint; (2) matching funnel and clamp. The filtration system is mounted on a metal stand with appropriate clamps and connected to a vacuum pump.

Figure 2. Filtration assembly (7.1.12)

7.1.13. Evaporator apparatus: Buchi Rotavapor™ (or equivalent), Neslab™ RTE-101 refrigerated recirculator (or equivalent) and a Savant™ SpeedVac™ Water jet vacuum (or equivalent).

Figure 3. Evaporator apparatus (7.1.13)



7.1.14. Nitrogen evaporator: Organomation™ N-Evap™ (or equivalent).
7.1.15. Nitrogen gas, lab grade or higher.
7.1.16. Class A volumetric pipettes.
7.1.17. Class A volumetric flasks.
7.1.18. Disposable glass Pasteur pipettes.
7.1.19. Balance: Sartorius R 160P Electronic Microbalance or equivalent capable of measuring to 0.01mg.
7.1.20. Chloroform: High purity high performance liquid chromatography (HPLC) grade, Optima or equivalent.
7.1.21. Sodium sulfate (if needed), baked at 425°C (±25°C) overnight.
7.1.22. Beakers to hold thimbles, baked at 425°C (±25°C) overnight.

7.2. Column Chromatography

7.2.1. Solvents: chloroform, benzene, iso-octane, methanol (High purity HPLC grade, Optima or equivalent).
7.2.2. Glass wool: Pyrex brand or equivalent, baked at 425°C (±25°C) overnight.
7.2.3. GF/A glass fiber filter paper, baked at 425°C (±25°C) overnight.
7.2.4. 7 mL clear glass vials with foil-lined caps, baked at 425°C (±25°C) overnight.
7.2.5. Syringe filters 0.45 µm PTFE, non-sterile.
7.2.6. Glass Luer-Lock syringe.
7.2.7. Graduated serological pipettes; 5mL, sterile, plugged, borosilicate glass, with cotton plug removed, baked at 425°C (±25°C) overnight.
7.2.8. Glass Pasteur pipets: baked at 425°C (±25°C) overnight.
7.2.9. Nitrogen evaporator: Organomation N-evap, or equivalent.
7.2.10. Nitrogen gas, lab grade or higher.
7.2.11. Labconco Centrivap Console, or equivalent.
7.2.12. Class A volumetric glass pipettes.

7.2.13. Class A volumetric glass flasks.
7.2.14. Handheld ultraviolet (UV) light
7.2.15. Alumina: 80–200 mesh, baked at 425°C (±25°C) overnight.
7.2.16. Silica gel: grade 62 and grade 923, acid washed for preparatory column chromatography and flash chromatography or equivalent, baked at 425°C (±25°C) overnight.
7.2.17. Mettler Toledo AX205 balance or equivalent (capable of measuring to 0.00001g).
7.2.18. Burette clamps.
7.2.19. Centrifuges: (7mL vials) Damon/IEC Division, model IEC Clinical Centrifuge, International Equipment CO, model CL or equivalent.
7.2.20. Centrifuge: (20mL and 40mL vials) International Equipment, size 2, model K#503P2 or equivalent.
7.2.21. Freezer: Thermo Scientific, model number 3552A or equivalent.

8. Procedure

8.1. Soxhlet Extraction

8.1.1. Rocks are ground to a fine powder (flour-like consistency) and extracted with 350mL chloroform at 55°C for at least 24 hours, or until the extract in the Soxhlet syphon tube is clear. Prior to extraction, boiling chips and two chloroform-rinsed strips of copper are placed in the round-bottom flask to remove elemental sulfur. The amount of rock used will depend on the richness of the rock being extracted. Lean rocks might require 50–150g while dark, sticky, hydrocarbon-smelling rocks and oil-stained sand may require less material (for example 0.1–10g).

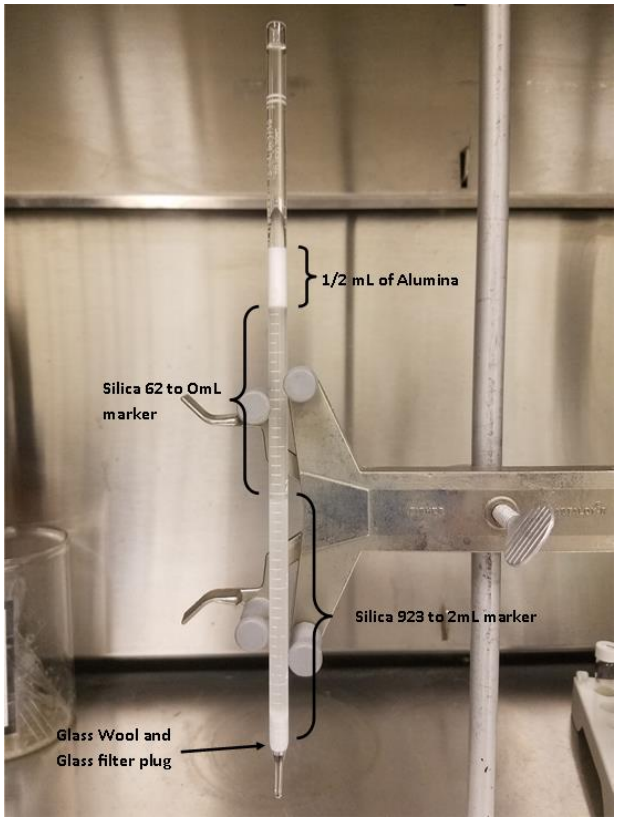
8.1.2. The extract is then filtered and concentrated down using a rotary evaporator (water bath temperature ~32°C, 18in.Hg vacuum). Once the volume of extract is reduced to a volume of approximately 1–5mL , the extract is transferred into a class A volumetric flask using a disposable transfer pipette and a known volume is removed using a class A volumetric pipette (typically 1–5mL), then dried and weighed to determine the concentration of bitumen in the rock (ppm, mg extract/kg rock). The size of volumetric flask used can vary greatly depending on the amount extract (sizes between 5mL to 250mL have been used); any size is acceptable as long as the extract meniscus at the volumetric marker line is visible.

8.2. Column Setup

Columns are made with 5ml disposable serological pipettes consisting of a glass wool and glass filter plug followed by a layer of silica gel grade 923 (~2mL) and a layer of silica gel grade 62 (~2mL) topped with a smaller layer of alumina (~1/2mL). The silica and alumina are activated by heating at 425°C for at least 12 hours. The silica 923 and 62 are then deactivated to 5% water (1:20 wt/wt) and the alumina to 1% water (1:100 wt/wt) in glass jars. The jars are capped, mixed, and allowed to equilibrate (let stand) for at

least 48 hours. Silica slurries are made by adding iso-octane to the silica and mixing in an Erlenmeyer flask that can be capped. The columns are assembled as shown in figure 4 below. The slurries are transferred into the column assembly using disposable glass pasteur pipettes. Once the columns are made, they are stored in iso-octane, in a capped glass graduated cylinder making sure the iso-octane level is above the top of the alumina layer.

Figure 4. Column Assembly



8.3. Asphaltene Precipitation-Rocks

A volume equivalent of a known mass of bitumen is transferred into a vial using a class A volumetric pipette (~100mg is desired but less can be used if not available) and reduced to 1mL using nitrogen evaporation. A solvent exchange is performed by adding 1mL of iso-octane to the bitumen, reducing the volume of the mixture to 1mL under nitrogen, then adding another 1mL of iso-octane. This is done a total of four times during which the asphaltenes will precipitate out of the solution. Once the solvent exchange is complete, an additional 6mL of iso-octane is added to the mixture which is then placed in a freezer overnight (~-25°C).

8.4. *Asphaltene Precipitation-Oils*

8.4.1. Oils are weighed directly into a clean 7mL vial; the optimal weight for an oil is ~100mg. Seven mL of iso-octane is added to the vial and mixed for about 30 seconds by vortex or sonication. The vial containing the mixture is then placed in a freezer overnight (~-25°C) to allow the asphaltenes to precipitate.

8.5. *Asphaltene Separation*

8.5.1. The mixture is centrifuged for 5 minutes to allow the asphaltenes to separate from the maltene. The maltene is then pipetted into a Luer-lock glass syringe fitted with a 0.45micron PTFE syringe filter. The filtered maltene is collected in a 30mL glass vial.

8.5.2. The asphaltenes are then rinsed by adding 1mL of iso-octane, vortexing the mixture, then repeating the steps described in 8.5.1. This is done three times, then the glass syringe and filter are rinsed three times with 1mL of iso-octane to remove any residual sample left on the assembly.

8.5.3. The asphaltenes remaining in the original 7mL vial are then placed under the syringe assembly and the filter is rinsed with 6–7mL of chloroform to remove any possible asphaltenes from the filter. The asphaltenes are then dried under a fume hood or with nitrogen evaporation and weighed.

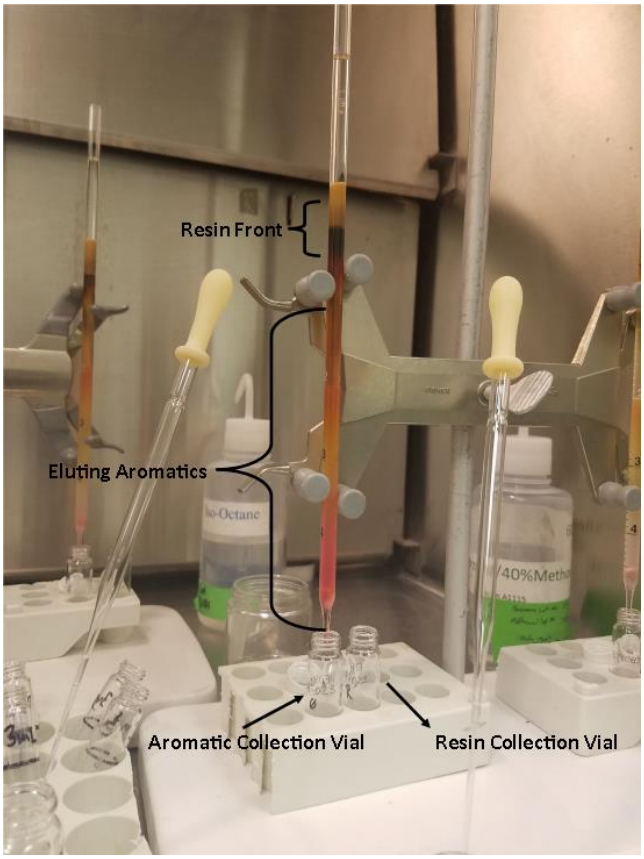
8.5.4. The maltene is reduced to 1mL under nitrogen evaporation in preparation for column chromatography.

8.6. *Column Chromatography and SARA analysis*

8.6.1. For the following steps, 7mL vials are used to collect each fraction. 1mL of maltene solution (Section 8.5.4) is introduced to the top of the column. The sample vial is rinsed three times with 1mL iso-octane, each rinse is added to the top of the column. An initial bed volume of 3mL is collected and disposed of. Saturates are eluted with iso-octane. Once 3mL of saturate eluate has been collected, the sample vial is rinsed three times with 1mL of benzene and added to the top of the column to begin eluting the aromatic fraction. The saturate eluate is collected until the aromatic front reaches the bottom of the column and then vials are switched to begin collecting the aromatic fraction. This usually can be easily observed as a yellow, red, or orange front, but a UV light may be used to view the aromatic front if it is difficult to see.

8.6.2. Once 3mL of aromatic eluate have been collected, the sample vial is rinsed three times with 1mL of 60/40 benzene/methanol azeotrope and introduced to the column. This will begin the elution of the resin fraction. The aromatic fraction is collected until the resin eluate reaches the bottom of the column. Vials are switched and the resin fraction is eluted with 60/40 benzene/methanol until 6–7mL have been collected. A typical column chromatography setup can be seen in figure 5 below.

Figure 5. Column Chromatography



8.6.3. The fractions are then dried by nitrogen evaporation, under a fume hood or with a Centrivap console. Resin and asphaltenes are placed in a fume hood or under a nitrogen evaporator until all the solvent has evaporated and the resins and asphaltenes are completely dry. More care is put into determining the final weight of the saturate, aromatic, and volatile fractions and while determining the bitumen concentration. For these fractions, the samples are placed in a fume hood or under nitrogen evaporation until it appears most of the solvent has evaporated. Then the sample is placed into a Centrivap for 15minute intervals, measuring the weight of the sample before and after each interval. The sample is considered dry and a final weight is determined once a difference of 0.3mg or less is observed for three consecutive measurements.

8.6.4. Once all fractions have been dried and weighed the percent SARA composition is calculated. When performing SARA analysis on an oil, the percent volatile composition (C15- Weight %) is calculated by taking an initial weight of an oil and placing it in a fume hood for 5–7 days to allow the volatiles to evaporate. They are

then placed in a Centrivap following the steps outlined in section 8.6.3 to determine the final weight. The difference between the "topped" oil (after volatile removal) and the original oil weight is then used to calculate the percent volatile composition to be included in the total % recovery.

8.6.5. Electrostatic charge around the glass vials and changes in ambient temperatures can result in errors in weight measurements and drift over time. For this reason, take steps to neutralize the static charge via a U-ionizer or similar technology, and it is suggested that the final weight and vial tare weight be measured on the same day. This can be done by obtaining the final weight dissolving the fraction in the appropriate solvent (saturates-iso-octane, aromatics-benzene, resins-60/40 benzene/methanol, bitumen and topped oil-chloroform), transferring it into a new vial and taking the tare weight of the original dry vial.

8.6.6. Formulas used to calculate the weight percentages are listed below. The total percent recovery for an oil is the sum of the SARA C15+ Weight percentages and the C15- Weight percent. For a rock, the C15+ Weight percent is the total percent recovery.

Calculation 1. C15+ Weight % (Oil)

$$\text{C15+ Weight \% (SARA fractions)} = \frac{Weight\ of\ Fraction\ (mg)}{((1-Fraction\ Volatile)\times Amount\ of\ Oil\ Used\ (mg))} \times 100$$

Calculation 2. C15- Weight % (Oil Volatiles)

$$\text{C15- Weight \% (Volatiles)} = \frac{Weight\ Untopped\ Oil\ (mg) - Weight\ Topped\ Oil\ (mg)}{Weight\ Untopped\ Oil\ (mg)} \times 100$$

Calculation 3. Total Weight % (Oil)

$$\text{Total Weight \%} = (C15 + Weight\ \%\ Saturates) + (C15 + Weight\ \%\ Aromatics) + (C15 + Weight\ \%\ Resins) + (C15 + Weight\ \%\ Asphaltenes) + (C15 - Weight\%)$$

Calculation 4. C15+ Weight % (Rock)

$$\text{C15+ Weight \%} = \frac{Weight\ of\ Fraction\ (mg)}{Amount\ of\ Bitumen\ Used\ (mg)} \times 100$$

9. Method Performance

9.1. SARA analysis by liquid column chromatography.

9.1.1. An oil from the Late Cretaceous (Cenomanian) J sand of the Dakota Group in the Denver-Julesburg basin was used to determine method performance. It is a light oil with an API gravity of 37 that has historically been used as a check standard at the U.S. Geological Survey's (USGS) Petroleum Geochemistry Research Laboratory. The data were collected over a period of 10 years, from two analysts and consisted of 53 replicates. The average, standard deviations, and interquartile (IQR = 3rd quartile – 1st quartile) ranges were calculated for each fraction. Outliers were identified as any parameter value falling outside of the range defined by 1st quartile – 1.5IQR and 3rd quartile + 1.5IQR. Thirteen out of the 240 results (50 runs × 5 fractions) determined were identified as outliers for values falling outside the range for either saturate, aromatic, resin, asphaltene, or volatile fractions (SARA C15+ Weight%'s and C15- Weight %). One volatile result exceeded the higher range while the rest of the outliers exceeded the lower range for various fractions. Samples containing one or more high or low outliers were removed from the pool and the coefficient of variation (COV, where COV=standard deviation/average) is used to assess the repeatability of each parameter.

9.1.2. The average weight percent and standard deviation of each SARA fraction, the volatile determination and the total percent recovery are listed in Table 1 for the J sand oil. The COV (0.20) was greatest with smallest weight percent fraction (1.8% for C15+ weight % asphaltenes). The COV (0.03) was smallest for the largest weight percent fraction (74.8% for C15+ weight % saturates). For all SARA fractions and the volatile determination, the COV increased with decreasing weight percent as seen in Table 1.

9.1.3. Raw data and results of SARA analyses for J sand oil are contained in Tables 2 and 3.

Table 1. Accuracy and Precision

	C15+ Weight % Saturates	C15+ Weight % Aromatics	C15+ Weight % Resins	C15+ Weight % Asphaltenes	C15- Weight % Volatiles	Total % Recovered
Average	74.8	18.8	3.4	1.8	25.3	99.1
Standard Deviation	2.4	1.5	0.5	0.4	1.6	2.3
COV	0.03	0.08	0.14	0.20	0.06	0.02

Table 2. Results For 40 Replicates

Run #	C15+ Weight % Saturates	C15+ Weight % Aromatics	C15+ Weight % Resins	C15+ Weight % Asphaltenes	C15- Weight % Volatiles	Total % Recovered
Run 1	68.6	19.5	3.0	2.0	24.5	94.7
Run 2	68.6	17.1	2.9	2.2	26.9	93.3
Run 3	74.3	19.5	3.3	1.4	25.0	98.8
Run 4	75.5	19.8	3.8	1.5	27.9	100.4
Run 5	75.6	19.8	3.7	1.4	29.6	100.3
Run 6	77.7	18.8	3.1	1.6	23.5	100.9
Run 7	73.8	19.6	2.2	1.6	26.6	98.0
Run 8	75.1	16.5	3.1	1.4	24.1	97.0
Run 9	79.3	17.7	2.9	1.2	23.3	100.9
Run 10	76.5	17.3	3.2	1.7	23.8	98.9
Run 11	76.0	18.7	3.2	1.3	24.1	99.5
Run 12	76.8	18.9	3.1	1.4	25.1	100.1
Run 13	74.0	19.1	3.5	1.8	27.4	98.9
Run 14	74.8	18.0	2.6	1.2	24.8	97.5
Run 15	72.5	20.3	3.2	1.6	26.7	98.2
Run 16	75.5	19.8	3.8	1.5	27.9	100.4
Run 17	77.5	20.2	3.5	1.6	25.7	102.1
Run 18	73.0	15.2	2.6	1.9	26.7	94.6
Run 19	74.9	21.0	3.3	1.9	26.3	100.8
Run 20	73.1	19.7	4.5	1.9	26.4	99.4
Run 21	78.3	19.8	3.5	2.1	26.9	102.6
Run 22	74.1	18.2	3.3	1.6	25.9	97.9
Run 23	78.2	20.2	4.1	2.1	26.2	103.4
Run 24	73.4	20.3	3.9	2.1	25.5	99.8
Run 25	78.0	20.4	3.8	2.7	26.9	103.5
Run 26	78.0	17.6	3.7	1.8	24.4	100.8
Run 27	74.3	18.8	3.5	1.8	23.9	98.8
Run 28	78.2	20.2	4.1	2.1	26.2	103.4
Run 29	74.1	17.4	3.5	1.5	22.6	97.4
Run 30	72.8	18.7	3.7	1.8	23.5	97.7
Run 31	72.2	21.0	3.9	1.7	25.1	99.1
Run 32	74.4	19.7	3.9	1.6	23.2	99.7
Run 33	74.1	14.9	3.5	1.9	22.6	95.8
Run 34	73.2	19.8	3.0	2.0	25.9	98.5
Run 35	73.9	18.7	3.4	2.4	25.5	98.8
Run 36	71.6	19.2	3.8	2.3	25.1	97.7
Run 37	74.4	17.6	3.2	2.2	25.4	98.1
Run 38	72.5	18.3	3.9	2.0	24.2	97.5
Run 39	76.5	17.4	3.8	2.3	24.3	100.0
Run 40	74.9	15.8	2.7	2.6	22.6	97.0

Table 3. Raw Weights

Run #	Amount of Oil Used (mg)	Weight Saturates (mg)	Weight Aromatics (mg)	Weight Resins (mg)	Weight Asphaltenes (mg)	Intial Weight Untopped Oil (mg)	Weight Topped Oil (mg)	Fraction Volatile (mg)/(mg)
Run 1	113.85	58.94	16.74	2.55	1.71	112.57	85.01	0.24483
Run 2	116.94	58.68	14.61	2.49	1.90	107.95	78.96	0.26855
Run 3	108.15	60.32	15.79	2.65	1.12	101.02	75.79	0.24975
Run 4	102.18	55.60	14.57	2.79	1.11	137.69	99.25	0.27918
Run 5	103.16	54.89	14.40	2.66	0.98	130.22	91.63	0.29634
Run 6	136.62	81.19	19.61	3.29	1.64	118.37	90.55	0.23503
Run 7	115.90	62.78	16.69	1.89	1.35	121.10	88.86	0.26623
Run 8	132.88	75.70	16.61	3.08	1.46	141.68	107.51	0.24118
Run 9	123.39	75.02	16.78	2.78	1.16	141.22	108.31	0.23304
Run 10	128.98	75.18	16.99	3.13	1.64	129.06	98.37	0.2378
Run 11	137.12	79.07	19.49	3.35	1.37	115.83	87.86	0.24147
Run 12	143.53	82.62	20.34	3.28	1.47	110.08	82.47	0.25082
Run 13	111.83	60.11	15.50	2.83	1.45	102.51	74.41	0.27412
Run 14	115.98	65.31	15.75	2.30	1.03	120.26	90.48	0.24763
Run 15	105.22	55.89	15.62	2.45	1.24	109.87	80.50	0.26732
Run 16	102.18	55.60	14.57	2.79	1.11	137.69	99.25	0.27918
Run 17	126.70	72.91	18.99	3.31	1.54	127.48	94.71	0.25706
Run 18	111.98	59.91	12.45	2.10	1.58	123.28	90.40	0.26671
Run 19	110.23	60.83	17.04	2.70	1.55	113.42	83.57	0.26318
Run 20	102.87	55.37	14.92	3.40	1.46	123.13	90.63	0.26395
Run 21	122.38	69.99	17.68	3.09	1.88	110.09	80.43	0.26942
Run 22	120.57	66.19	16.28	2.93	1.40	131.45	97.44	0.25873
Run 23	117.91	68.04	17.58	3.56	1.84	103.13	76.13	0.26181
Run 24	103.95	56.84	15.70	3.01	1.59	121.06	90.13	0.25549
Run 25	119.51	68.10	17.79	3.28	2.37	124.90	91.26	0.26934
Run 26	130.05	76.69	17.33	3.60	1.78	132.82	100.44	0.24379
Run 27	123.89	70.09	17.77	3.29	1.69	130.45	99.28	0.23894
Run 28	117.91	68.04	17.58	3.56	1.84	103.13	76.13	0.26181
Run 29	136.93	78.58	18.47	3.75	1.63	102.25	79.14	0.22601
Run 30	130.74	72.84	18.71	3.69	1.77	118.68	90.77	0.23517
Run 31	99.34	53.73	15.60	2.93	1.26	127.79	95.76	0.25065
Run 32	116.97	66.86	17.67	3.54	1.47	127.68	98.06	0.23199
Run 33	126.51	72.57	14.64	3.46	1.90	116.14	89.90	0.22593
Run 34	136.14	73.79	19.95	3.03	2.04	106.82	79.13	0.25922
Run 35	138.04	76.03	19.27	3.48	2.45	113.72	84.73	0.25492
Run 36	131.51	70.49	18.93	3.77	2.30	128.25	96.06	0.25099
Run 37	128.49	71.28	16.90	3.02	2.13	118.97	88.70	0.25443
Run 38	131.71	72.39	18.25	3.94	2.01	102.97	78.09	0.24162
Run 39	113.64	65.82	14.93	3.24	1.96	94.83	71.76	0.24328
Run 40	100.95	58.53	12.37	2.10	2.05	101.33	78.42	0.22609

9.2. Determination of bitumen concentration by Soxhlet extraction.

9.2.1. Samples taken from two USGS shale geochemical reference materials (GRMs), ShBOQ-1 and ShMCO-1, were extracted to determine the reproducibility and

repeatability of determining the bitumen concentration or EOM by Soxhlet extraction (the first step in SARA analysis of a rock). ShBOQ-1 was selected to determine variability in a sample containing high concentrations of bitumen (0.89wgt%). ShMCO-1 was selected to determine the variability in a sample with low concentrations of bitumen (0.15wgt%). For more information on GRM's see Birdwell and Wilson, 2019. The bitumen concentrations were calculated in ppm (mg bitumen/kg rock).

9.2.2. The average bitumen concentration (EOM, average ± COV%) of ShBOQ-1 was determined to be 8857 ppm $\pm$ 3% and for ShMCO-1 the average bitumen concentration was determined to be 1477 ppm $\pm$ 5%. See Tables 4 and 5 below for results, reproducibility and repeatability.

Table 4. Results for Replicates

Sample Run	EOM ppm (mg/kg)	Sample Run	EOM ppm (mg/kg)
ShBOQ-1_1	8519	ShMCO-1_1	1390
ShBOQ-1_2	9022	ShMCO-1_2	1535
ShBOQ-1_3	9133	ShMCO-1_3	1388
ShBOQ-1_4	8903	ShMCO-1_4	1376
ShBOQ-1_5	8965	ShMCO-1_5	1547
ShBOQ-1_6	8661	ShMCO-1_6	1364
ShBOQ-1_7	9064	ShMCO-1_7	1494
ShBOQ-1_8	9132	ShMCO-1_8	1472
ShBOQ-1_9	8913	ShMCO-1_9	1592
ShBOQ-1_10	8876	ShMCO-1_10	1499
ShBOQ-1_11	9147	ShMCO-1_11	1563
ShBOQ-1_12	8841	ShMCO-1_12	1543
ShBOQ-1_13	8351	ShMCO-1_13	1433
ShBOQ-1_14	8464		

Table 5 Reproducibility and Repeatability

	ShBOQ-1 EOM ppm (mg/kg)	ShMCO-1 EOM ppm (mg/kg)
Average	8857	1477
Stdev	252	76
COV (%)	3	5

10. References

Birdwell, J.E. and Wilson, S.A. 2019. Variability in Results from Mineralogical and Organic Geochemical Interlaboratory Testing of U.S. Geological Survey Shale Reference Materials. Unconventional Resources Technology Conference, Denver, CO, July, paper no. 457, 19p, accessed (3/20/2020) at DOI 10.15530/urtec-2019-457.