SRA User Guide

Source Rock (SR) Analyzer: User Guide from (SRA_UG_371T_draft)

Manual Information

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Introduction

This user guide contains standard operational procedures for the Source Rock Analyzer (SRA). The chemistry laboratory technician performs maintenance and configuration of the SRA. Information for the laboratory technician is presented in the *SRA Analyzer Advanced User Guide.???* *[Ithink that we should combine the two. EM][Agreed DJH]*[DH1]

[DH1]Erik and/or Lisa, Vinny indicated that he is not familiar enough with the inner workings of the SRA to do a thorough revision of the AUG (and combination with the UG, I still agree with that), so I'm leaving this for you guys to work on together. (To complete 31 December 2017.)

Method Overview

Pyrolysis analysis is conducted on dried ground sediments or rock for the purpose of safety monitoring. The analysis yields information about thermal maturation, source of hydrocarbons and petroleum potential.

Method Theory

The pyrolysis method consists of programmed temperature heating in a pyrolysis oven of a sample (80 – 100mg), in an inert atmosphere (helium), to quantitatively determine free hydrocarbons contained in the sample and the hydrocarbon- and oxygen-containing compounds that are volatilized during the cracking of unextractable organic matter (kerogen).

Pyrolysis data may be compromised in samples containing greater than 10 wt% carbonate and for young (<1 Ma) samples or very immature organic matter (T_{max} < 400°C). Samples with less than 0.5 wt% TOC may not give reliable results because of the small size of the S1, S2, and S3 signals.

Data Values

The data obtained from the TPH-TOC analyses are defined by the following parameters

- S1, S2, S3, S4
- Tmax
- Total Organic Carbon (TOC)
- Hydrogen Index (HI)
- Oxygen Index (OI)
- Production Index (PI)
- S1/TOC

S1 Parameter

S1 (milligrams of hydrocarbon per gram of rock) is an indication of free hydrocarbons (gas and oil) in the sample. S1 > 1 may be indicative of an oil show. S1 normally increases with depth. S1 is measured via an FID (Flame Ionization Detector).

Free thermally extractable hydrocarbons in the rock sample that vaporize at temperatures up to ~ 330°C are included in S1. Heavier, free hydrocarbons and nonhydrocarbons that vaporize or crack at higher temperatures are included in the S2 peak .

S1 can be elevated by contamination from organic drilling fluid additives such as diesel, walnut shells, Qwik-Seal, Lubra beads, gilsonite, etc. Nonindigenous hydrocarbons expelled from source rocks elevate the S1 value in a reservoir rock. To convert S1 to ppm, multiply the S1 value by 1000. To convert the original S1 value to an approximate barrels of oil per acre foot, multiply by 20.082.

S2 Parameter

S2 (milligrams of hydrocarbon per gram of rock) hydrocarbons result from the cracking of kerogen and high molecular weight free hydrocarbons that do not vaporize in the S1 peak. S2 is an indication of the quantity of hydrocarbons that the rock has the potential of producing should burial and maturation continue. This parameter normally decreases with burial depths >1 km.

To convert to ppm, multiply the S2 value by 1000. To convert the original S2 value to an approximate barrels of oil per acre foot, multiply by 20.082.

T_{max} (°C) Parameter

This is the temperature of maximum rate of evolution of S2 hydrocarbons (top of S2 peak). T_{max} indicates the stage of maturation of the organic matter. T_{max} values are affected by low organic matter content where low S2 peaks are encountered. When the S2 value is < 0.5 and the S2 peak does not have a definitive peak (i.e., is broad and flat), T_{max} values may not be reliable. Also, organic-lean clayey sediments with S2 values as high as 2.00 may have unreliable T_{max} values values.

T_{max} may be affected by the presence of heavy free hydrocarbons in the S2 peak, which may cause T_{max} to be anomalously low (<400°C). Also, T_{max} may be affected by reworked organic matter or salt ionization, which may cause T_{max} to be anomalously high (>550°C).

T_{max} values and true T_{max} temperatures vary with the temperature programming rate and are useful for approximating kinetic values. T_{max} is a calibrated temperature and does not represent the true (absolute) temperature.

Maturation of organic matter can be estimated by the T_{max} range:

- T_{max} = 400°–430°C: immature organic matter
- T_{max} = 435°–450°C: mature or oil zone
- T_{max} > 450°C: overmature zone

S3 Parameter

S3 (milligrams of organic carbon dioxide per gram of rock) is produced during pyrolysis of kerogen and is organic carbon dioxide evolved during low-temperature pyrolysis (<390°C). It may be affected by the decomposition of inorganic matrix particularly due to weathering or mineral matrix interaction. S3 is measured via the CO_2 detector on the SRA. Generally, S3 values >200 are anomalously high, possibly due to high concentrations of carbonates that break down at temperatures <390°C and may or may not be valid. S3 is an indication of the amount of oxygen in the kerogen and is used to calculate the oxygen index [see Oxygen Index (OI) Parameter].

S4 Parameter

S4 (milligrams of carbon per gram of rock) is obtained from oxidizing (at 600°C) the organic matter remaining in the sample after pyrolysis (residual carbon). Using this value, TOC is determined by adding the residual organic carbon to the pyrolyzed organic carbon. It is measured using a combination of the CO and CO_2 detectors. Because the instrument automatically combines convertible carbon (pyrolyzed carbon) with the residual carbon (RC) and reports TOC to actually determine the S4 value, it is necessary to subtract the convertible carbon from the TOC.

$$S4 = 10 \times TOC - [0.83 \times (S1 + S2)]; RC = S4/10$$

TOC Parameter

TOC is the weight percent of carbon (unit weight of carbon per unit weight of whole rock). TOC is composed of convertible fraction, which represents the hydrocarbon already generated (S1) and the potential to generate hydrocarbons (S2). The residual fraction (S4) has no potential to generate hydrocarbons.

$$TOC = PC + RC$$

$$TOC = [k \times (S1 + S2)]/10 + S4/10$$

Where PC = Pyrolyzed Carbon, RC = Residual Carbon, k = .83 (an average carbon content of hydrocarbons by atomic weight).

Hydrogen Index (HI) Parameter

HI is the normalized hydrocarbon content of a rock sample. Kerogen type information is derived from this value as follows:

- Type I kerogens are hydrogen rich
- Type III kerogens are hydrogen poor
- Type II kerogens are intermediate between Type I and Type III

HI decreases as the sample matures. HI may be lowered by weathering or mineral matrix interactions, which cause reduction in the S2 value. Marine organisms and algae, in general, are composed of lipid- and protein-rich organic matter, where the ratio of H to C is higher than in the carbohydrate-rich constituents of land plants. HI typically ranges from ~100 to 600 in geological samples. High HI values (>400) indicate large proportions of well-preserved algal and microbial organic matter.
HI = (S2 * 100)/TOC

Oxygen Index (OI) Parameter

OI is the normalized oxygen content of a rock sample. Type III kerogens generally have higher OI than either Type I or II kerogens. However, the hydrogen content is the principal discriminating factor for oil or gas potential. OI may be increased by weathering or mineral matrix interactions, which elevate the S3 value. If TOC is <0.50 wt%, OI may be meaningless (Espitalié, 1982). OI correlates with the ratio of O to C, which is high for polysaccharide-rich remains of land plants and inert organic material encountered as background in marine sediments. OI values range from near 0 to ~150. High OI values (>100) are an indicator of continental organic matter or immature organic matter from all sources.
OI = (S3 ¿ 100)/TOC

Production Index (PI) Parameter

PI is indicative of the conversion of kerogen into free hydrocarbons or, in a general sense, the transformation ratio. PI increases with increasing thermal maturation in the absence of expulsion. Anomalies may be due to differences in organic facies or migration into or expulsion out of a sediment sample. PI values indicate the following:

- PI < 0.2: immature rocks
- PI = 0.3–0.4: typical for samples in the petroleum window
- PI > 0.5: may indicate proximity of migrated hydrocarbons or trapped petroleum
  - PI = [S1/(S1 + S2)] x 100

S1/TOC Parameter

The ratio of free hydrocarbons (S1) to TOC may be used to identify source or reservoir rocks. The S1 determination yields lighter hydrocarbons, which are usually lost during solvent evaporation.. This parameter can be evaluated as follows:

- Source rocks have above average S1/TOC ratios
- Reservoir rocks have very high S1/TOC ratios

Evaluation requires assessment of possible contamination by drilling fluid additives and regional geochemistry of sediments.

$$S1 \times 100/TOC$$

Apparatus, Reagents, & Materials

SRA Hardware

The SRA system consists of the following main components (*Figure 1*):

- Autosampler
- Main control unit: oven and detector temperature control units and gas flow controllers
- Infrared (IR) section : CO/CO_2 detectors
- Combustion with gas separation and FID (pedestal, oven, and conversion FID)

Figure 1: The four main components of the SRA

Figure 2. SRA Sample Preparation Tools.

Laboratory Equipment
- Cahn analytical balance (Analytical Balance User Guide)
- SRA
- Laboratory apparatus for sample preparation

Reagents

Compressed gases

- Hydrogen, 60–80 psi
- Helium, 60–80 psi
- Air, laboratory grade, 60–100 psi

Standards

- Standard material (99986)
- Weatherford Standard 533 (PWDR3998091)

Instrument Calibration

Every time the instrument is powered on, the SRA must be calibrated (standard run as a 'calibration' type. After this initial calibration, and if no other changes are made to the instrument, a only a blank and a standard check need to be measured to verify calibration. Allow the instrument to stabilize for 3 hrs before performing a calibration.

Sample Preparation

Sediments and sedimentary rock samples logged into the LIMS system as **SRANL** are analyzed by SRA. During sample preparation, keep in mind that sample container numbers must correlate with autosampler place numbers. Sample preparation includes the following steps:

- Freeze-dry sample
- Grind and homogenize sample
- Weigh sample
- Place sample in a crucible in the autosampler tray

Drying and Grinding Samples

1. Obtain freeze-dried bulk sample.
2. Crush sample by hand or use an electric mill to roughly crush samples.
3. Homogenize sample using a mortar and pestle. **Note**: Inadequate homogenization will cause high standard deviation in the data.

Text ID (parent)	Text ID (child)	Mass	Container number	LIMS code	SRA code
Blank			1		BLK
STD99986	OTHR137987	90.00	2	QAQCSTD	STD
OTHR2764599	OTHR346972	92.00	3	UNK	TPH
OTHR2765092	OTHR130746	92.36	4	UNK	TPH
CV2-99986	OTHR427034	92.05	10	QAQCCV	TPH

Weighing Samples

See *Quality Assurance/Quality Control* for sample amounts and explanation of sample codes.

1. Log the samples in the blue book as follows:

- **text ID**
- **mass**: sample amount weighed into crucible (80 - 100mg)
- **container number**: same as autosampler tray slot number the sample will be placed in

- **SRA code**:
  BLK: calibration blank
  STD: calibration standard
  TPH: unknown sample, QA/QC check (TPH stands for total petroleum-hydrocarbon)

1. Wipe sample filler, spatula and forceps.
2. Log into the balance system for Cahn balance.
3. Select **Source Rock Analyzer**.
4. Enter **Text ID** and **Container Number**. The Text ID for STD 533 is PWDR3998091.
5. Set **Measurement count** to 200 or 300 depending on sea state.
6. Place a weighing paper boat on each balance pan. Close door. Click **Tare**.
7. Once the tare is complete, place 80-100 mg of sample in the weighing paper boat in the left pan. Click **Weigh Sample**.
8. Once weighing is complete, write weight in log book and click **Save**.
9. Place weighed sample material in a crucible using sample filler.

Sample Analysis

Sample analysis workflow is as follows:

- Prepare the instrument (see *Preparing the SRA Instrument*).
- Set up software for sequence acquisition (see *Setting up the Software*).
- Acquire samples (see *Running Samples*).

Preparing the Instrument

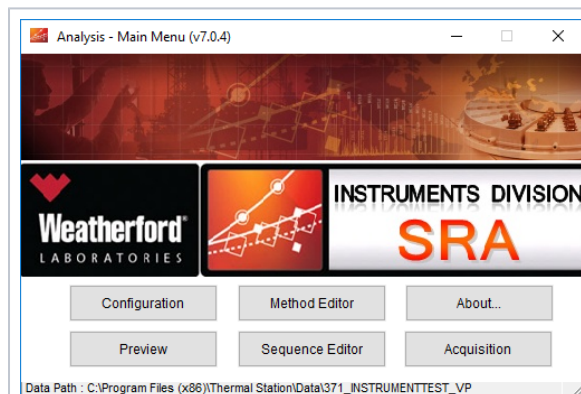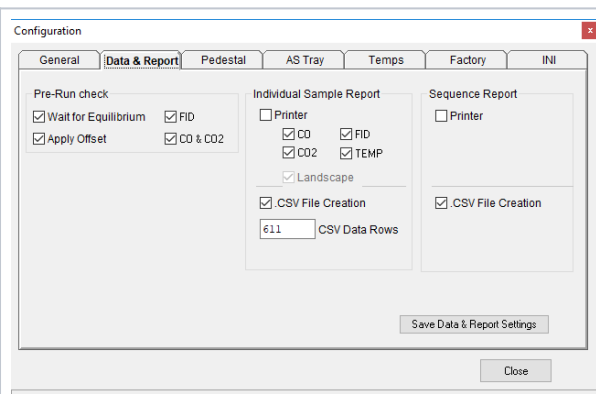**Figure 3: Acquisition software main screen**

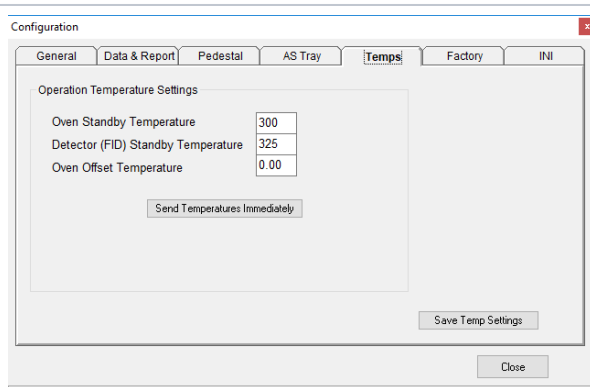**Figure 4: Data and Report tab of the Configuration Menu**

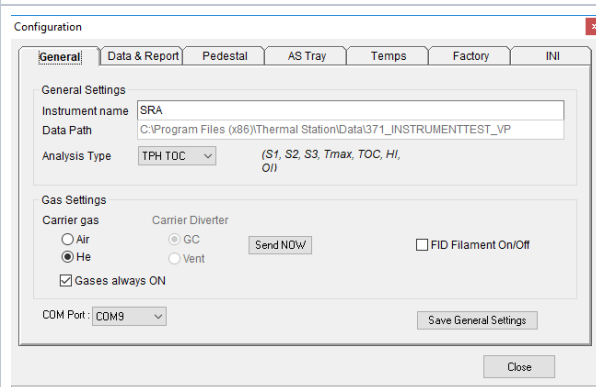**Figure 5: Current/standby temperature settings**

Figure 6: General Tab of the Configuration Menu

SRA Instrument

The SRA goes through an intense warm-up for at least six hours before operation. Perform the following steps to prepare for sample acquisition

1. Open H_2, He, and air gas lines. **Note**: Verify gas gauge pressures using the gas flow meter.
2. Turn on the SRA.
3. Turn on the PC.
4. Double-click the **TStationAcq.exe** shortcut icon on the desktop to open the software *Main Menu* (*Figure 3*).
5. Check gas flow rates by removing the instrument panel covering the FID castle (*Figure 7*). Gas flow rates can be manipulated by rotating the valves on the rear of the instrument IR Section.
   a. Disconnect each gas line individually. Verify the hydrogen flow rate is ~65 mL/min, and the air flow rate is ~300 mL/min with a flowmeter. Use a Swagelock fitting to connect the flowmeter line with the instrument. Reconnect the gas line.
   b. Disconnect the gas line at the base of the oven pedestal (*Figure 8*) and connect to the flow meter. Navigate to Configuration>General and verify the helium flowrate is 100 mL/min and the oxidation air flowrate is 250 mL/min by selecting the gas radio buttons (*Figure 6*). Reconnect the gas line.
6. Zero and calibrate the CO/CO_2 detectors. This step should only be performed after the instrument has had ample time to warm up and clean, moisture-free helium has been circulating through the pedestal for at least 5 minutes.
   a. Open the IRCal program and click the play button (*Figure 10*).
   b. Calibrate the zero point of the IR sensor by clicking the lock icon (to activate the calibration buttons) and clicking **Zero**. The readings should be between 0-200 ppm before zeroing.
   c. Disconnect the fitting at the base of the drierite moisture trap located on the left side of the instrument and connect the 1% carbon monoxide gas standard bottle to the line entering the instrument (*Figure 9).*
   d. After 3-4 minutes the readings should stabilize. Click **Calib** and the reading should revert to 10000 ppm (1% wt). Click the lock icon to deactivate the zero and calib buttons.
   e. Reconnect the moisture trap, then perform steps a-e again to calibrate the IR cell for carbon dioxide after residual carbon monoxide has been purged from the IR cell (~5 mins).
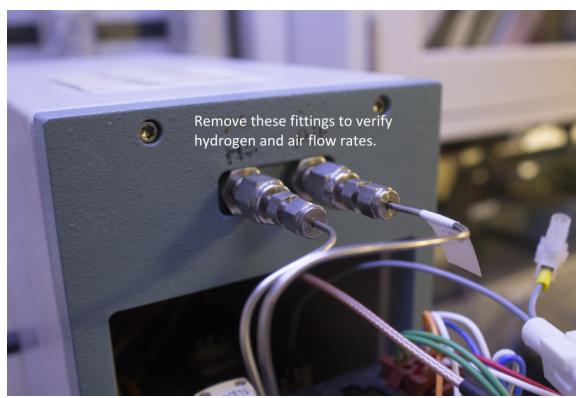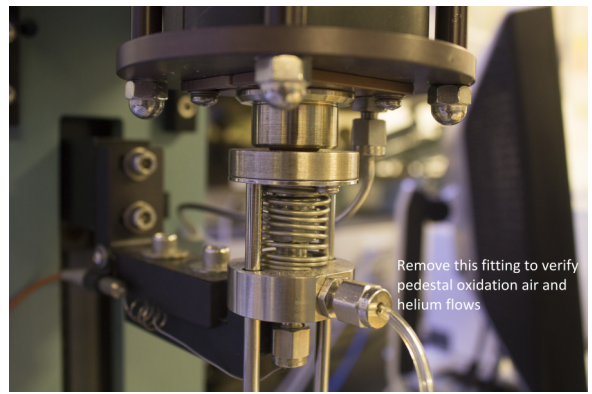
Figure 7: Hydrogen and air supply lines to the FID

Figure 8: Sample pedestal and gas line for purge gas (helium) and oxidation air

Figure 9: Setup of the IR cell calibration
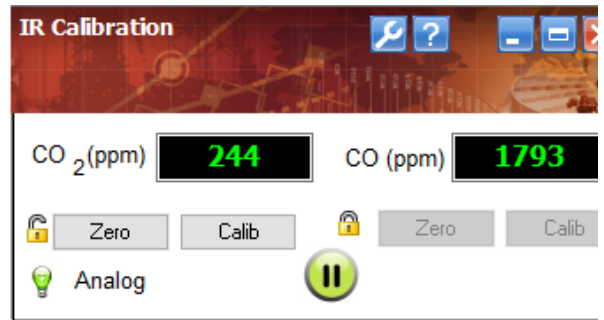

Figure 10: IR Calibration screen

Setting up the Software

Prepare the software for data acquisition as follows:

- Create a data folder
- Edit the method (if needed)
- Edit the sequence table

Creating a New Folder

Data files are saved into the expedition-specific data folder with respect to each sequence .

- Open the Data folder at C:\Program Files\Thermal Station\Data.
- Create a new folder named EXPxxx where xxx is the expedition number

Editing the Method

The method does not need to be edited for regular onboard measurements (i.e., safety monitoring) except for the standard information. The Technician will edit the fields in the **Standard** tab (*Figure 12*) if the standard material changes. In that case, one blank, one standard, and one known sample (house standard) must be measured to confirm calibration (see *Quality Assurance/Quality Control*).

**Figure 11: Method Editor temperature program menu**

Figure 12: Method Editor standard input menu

Editing the Sequence Table

A sequence table represents an analytical batch (see *Quality Assurance/Quality Control* for information about batches and calibration). The sequence file is an archive file that is updated with respect to each run. After each batch, the sequence table is saved into the expedition-specific data folder. A typical sequence table contains the following (see *Figure 9*):

- *Data File* name (one for each sample to be run). Examples:
- Calibration blank: BLANK
- Calibration standard: 88695, 533
- Calibration verification standard: STDCHK
- Unknown samples: textID = LIMS text ID
- *Sample ID:* must be identical to the Text ID.
- *Method*
- *C#:* container number (must match autosampler place number
- *Sample Weight:* (mg)
- *Acq Type:* acquisition type
- BLK = Calibration blank
- STD = Calibration standard
- TPH = Unknown samples or QA/QC control samples
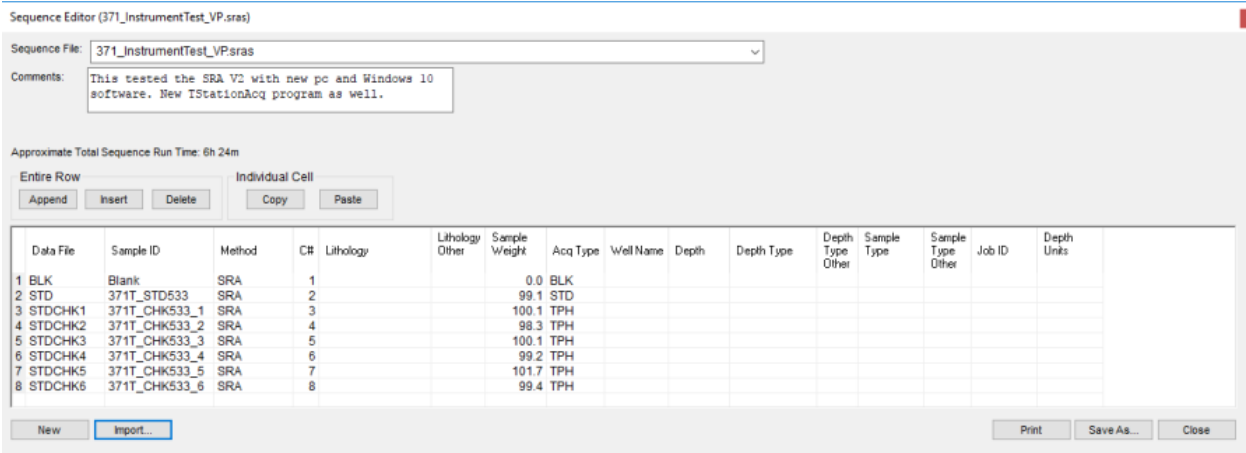
Figure 13. SRA > Sequence Editor > Sequence Table.
Edit the sequence table as follows:

1. Click **Sequence Editor** on the *Main Menu* (*Figure 3*).
2. Fill in the *Data File, Sample ID, Method, C# (container number), Sample Weight*, and *Acq Type* (blank - BLK, calibration – STD and unknown samples – TPH), fields using the logbook as the reference.
3. Click **Save As** and give the sequence a new name.

Running Samples

To analyze samples, fill in the *Acquisition Setup* screen and confirm sample information on the *Analysis* screen.

1. Select Main Menu > **Acquisition** to open the Acquisition Setup screen (*Figure 14*).

- *Operator*: operator's last name. This name is the key to access LIMS.
- *Sample Selection*: select the samples to be run from the list shown on the screen.

1. Specify the data folder:

- Select parent folder **EXPxxx** from the explorer window on the screen.
- Enter subfolder name **EXPxxx_sequence number** (e.g., **EXP777_1**, **EXP777_2**) in Data Folder field.

1. Click **Next** to open the Analysis screen (*Figure 15*).
2. Click **Info** at the bottom right to open detail information and confirm the information for the first sample.
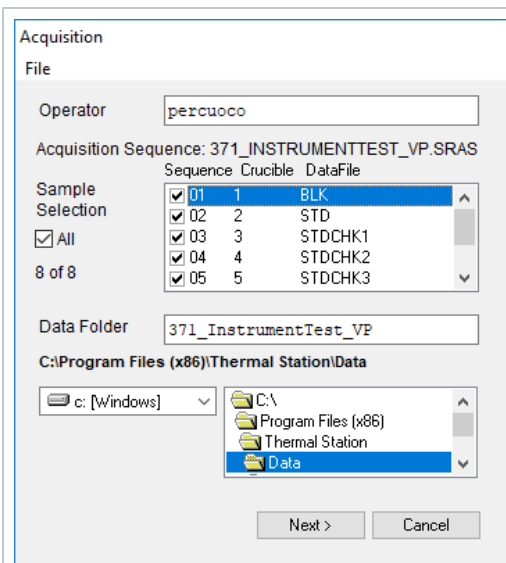3. Click **Start Sequence** above the sample window to start the run.
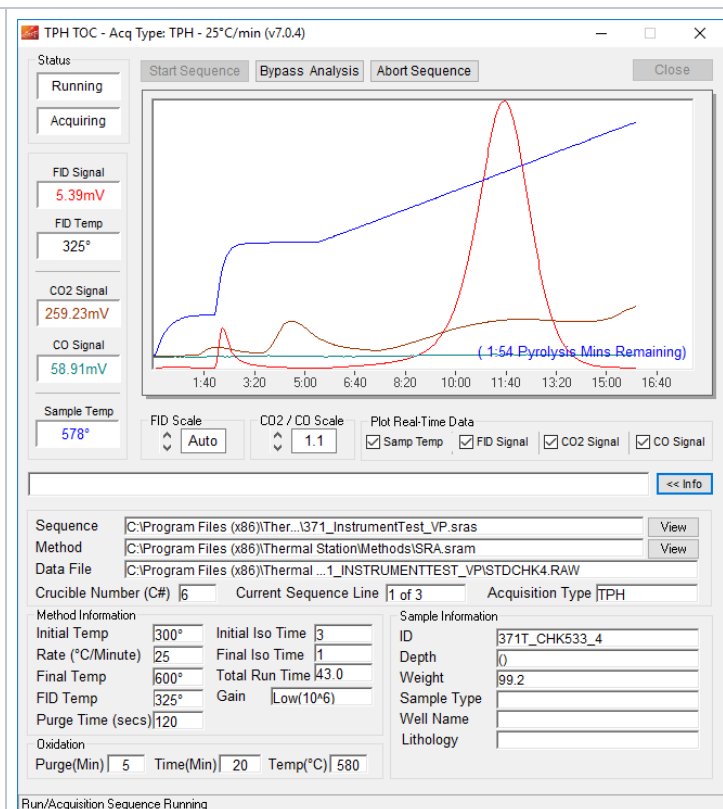
Figure 14. SRA > Acquisition.

Figure 15. Analysis Screen.

Analyzing results

The sequence results may be viewed individually by opening up the RAW files stored in the data directory with the TStationProc program. A graphical display of the oven temperature, FID, CO2, and CO data streams is presented. Typically, trends in these data will appear similar to those for Weatherford Standard 533 as shown in *Figure 16*. Additional measurement parameters may be viewed by clicking the **Details** button (*Figure 17*). This information may be exported from TStationProc or reprocessed by navigating to **File>Export** or **File>Reprocess** Sequence, respectively.

Figure 16: TStationProc program menu with sample raw file loaded

Figure 17: TStationProc detailed overview
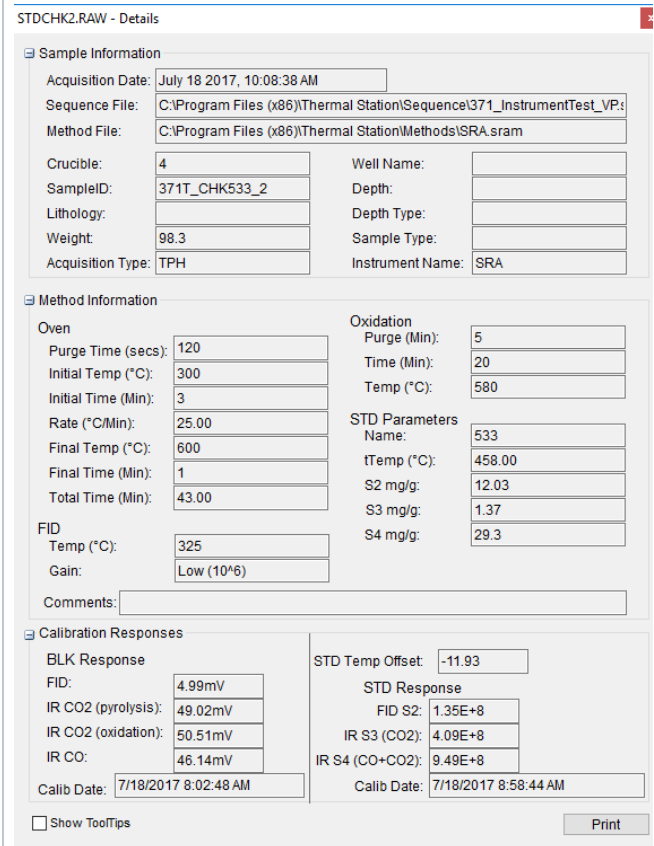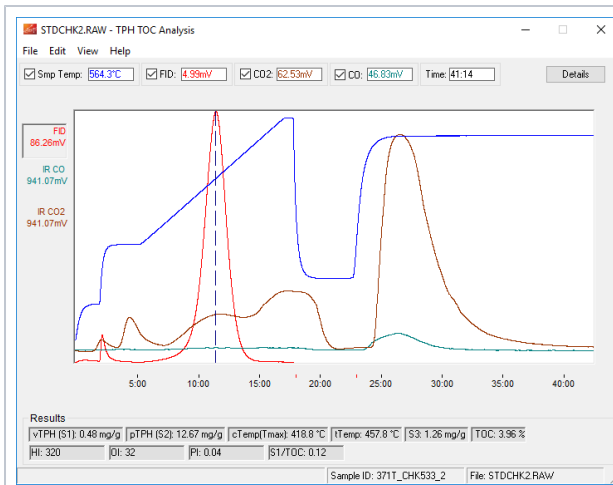
Quality Assurance/Quality Control

Analytical Batch (Sequence)

An analytical batch is referred to as a Sequence in this User Guide. Each sequence can contain the following samples:

- Calibration blank (CB): A crucible containing no material and included as the first sample of any sequence
- Calibration standard (CS): ~90-100 mg of standard material run immediately after the calibration blank, and used to calibrate the instrument signals to known values
- QA/QC standard (CV) : A standard run as a sampler which allows the user to monitor instrument accuracy and precision. Calibration verification is conducted for each batch of 10 samples:
- QA/QC blank: An empty crucible analyzed as a sample
- Unknown sample(s) (TPH): ~90-100 mg of freezed-dried, powdered sample material

Analyte	Standard 999986	Standard 533
S1 (mg HC/g)	0.16 ± 0.08 (50%)	0.76 ± 0.19 (25%)
S2 (mg HC/g)	8.41 ± 1.26 (15%)	12.21 ± 1.83 (15%)
S3 (mg CO2/g)	0.39 ± 0.10 (15%)	1.42 ± 0.36 (25%)
S4 (mg C/g)	23.99	29.3
Tmax (°C)	418 ± 5	418 ± 5
TOC (wt%)	3.11	3.78

Precision

Precision of analysis is determined by calculating the relative standard deviation of replicate samples.

Accuracy

Accuracy is determined by running a calibration verification (CV) with every batch or every 10 samples, and calculating the percent difference of measured values from known values.

LIMS Integration

Results are stored in the LIMS database associated with an analysis code and an analysis component, component value, and component unit. Analysis codes and their components, definitions, and units are listed below. Use Spreadsheet Uploader to transfer data from a Sequence Report to LIMS. Complete fields in Spreadsheet Uploader with the following parameters: Analysis: SRANL, Instrument: SRA, Display Flag: T, and the rest according to the table below.

Table 1: LIMS components and units

Analysis	Component Name	Definition	Unit	LIMS Unit
SRANL	HI	Hydrogen index (S2 x 100/TOC)	mg HC/g TOC	NONE
	OI	Oxygen index (S3 x 100/TOC)	mg CO_2/g TOC	NONE
	PC	Pyrolysis carbon (0.83 x [S1 + S2]/10)	mg HC/g rock	MG_PER_G
	PI	Production index ([S1/(S1 + S2)] x 100)	—	NONE
	S1	HC vaporize < 330°C (free oil)	mg HC/g rock	MGHC_P_GC
	S2	HC vaporize > 330°C (kerogen)	mg HC/g rock	MGHC_P_GC
	S3	Carbon dioxide evolved	mg CO_2/g rock	MGHC_P_GC
	S4	Residual carbon	mg HC/g rock	MGHC_P_GC
	mass	Sample mass	Mg	MILLIGRAMS
	tmax	Maximum S2 (peak) temperature	°C	CELSIUS
	toc	Total organic carbon	wt%	PCT_WEIGHT

Health, Safety, & Environment

Safety

All Technicians must adhere to the complete required safety protocols operating the SRA instrument.

Compressed Gases

- Always wear safety glasses when handling and using compressed gases. Read the MSDS information for the gases used in this procedure.
- Hydrogen gas (CAS 1333-74-0) is highly flammable, explosive limits in air = 4%–74%. Be careful with ignition sources and oxidizers.
- Helium gas (CAS 7440-59-7) is inert but may cause suffocation by displacing oxygen in the air during a release.
- Carbon monoxide gas can cause headaches, dizziness, nausea, unconsciousness and even death of exposure is unmitigated. Ensure instrument ventilation lines are routed to a fume hood when performing the carbon monoxide calibration.
- Check for leaks in compressed gas lines.
- Ground all equipment and lines associated with hydrogen usage.

High Temperatures

- High oven and detector temperatures (325°–600°C) are reached during operation. Use proper heat protective equipment when operating the instrument.
- Make sure the FID cover is always installed during operation to protect from burns.

Instrument Safety Features

- The instrument will sound an audible alarm if a gas cuts off. Check gas flow and tank pressure if the alarm sounds.

Pollution Prevention

- Trace amounts of pyrolysis products are consumed by the flame ionization detector.
- Helium gas has no adverse ecological effects.

Waste Management

- The sample after pyrolysis can be disposed of in the burnable trash bin.
- Sample crucibles are reused. The crucibles can be cleaned in a water/ethanol mix, sonicated for a couple of hours and properly rinsed, or heated to 600°C in the muffle furnace.
- Unused quantities of compressed gases are stored in labeled cylinders with protection cap in place until return to manufacturer.