SRA User Guide

- Manual Information
- Introduction
 - Method Overview
 - Method Theory
 - Data Values
 - S1 Parameter
 - S2 Parameter
 - Tmax (°C) Parameter
 - S3 Parameter S4 Parameter
 - TOC Parameter
 - Hydrogen Index (HI) Parameter
 - Oxygen Index (OI) Parameter
 - Production Index (PI) Parameter
 - S1/TOC Parameter
- Apparatus, Reagents, & Materials
 - SRA Hardware
 - Laboratory Equipment
 Reagents
 Standards
- Instrument Calibration
- Sample Preparation ٠
 - Drying and Grinding Samples
 - Weighing Samples
- Sample Analysis
 - Preparing the Instrument
 SRA Instrument
 - Setting up the Software
 - Creating a New Folder
 Editing the Method
 - Editing the Sequence Table
 - Running Samples
 - Analyzing results
- Quality Assurance/Quality Control
 - Analytical Batch (Sequence) • Precision
 - Accuracy
- LIMS Integration
- Health, Safety, & Environment
 - Safety
 - Compressed Gases
 - High Temperatures
 - Instrument Safety Features
 - Pollution Prevention
 - Waste Management
- LIMS Component Table
- Archive Versions

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

Manual Information

| Author(s): | K. Fujine | | |
|---------------------------------------|--|--------------|-------------------------|
| Reviewer(s): | L. Brandt | | |
| Manager Approval (Name, Title, Date): | D.J. Houpt | | |
| Audience: | Scientists, Laboratory Technicians | | |
| Origination date: | 5/12/08 | | |
| Current version: | V1.0 | 8/20/13V371T | July 2017 (V. Percuoco) |
| RevisedPrevious versions: | 5/5/15 E. Moortgat, 7/21/17 V. PercuocoV1.0 | 8/20/13 | |
| Domain: | Chemistry | | |
| System: | Rock Maturity | | |
| Keywords: | Rock-Eval, Tmax, Source Rock, Hydrocarbon Maturity | | |

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.

 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:

• $T_{\text{max}} = 400^{\circ} - 430^{\circ}$ C: immature organic matter

- T_{max} = 435°-450°C: mature or oil zone
- $T_{\text{max}} > 450^{\circ}\text{C}$: 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 lowtemperature 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 CO₂ 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 x TOC - [0.83 x (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.

$$TOC = PC + RC$$

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

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

Ol is the normalized oxygen content of a rock sample. Type III kerogens generally have higher Ol than either Type I or II kerogens. However, the hydrogen content is the principal discriminating factor for oil or gas potential. Ol may be increased by weathering or mineral matrix interactions, which elevate the S3 value. If TOC is <0.50 wt%, Ol may be meaningless (Espitalié, 1982). Ol 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. Ol values range from near 0 to ~150. High Ol values (>100) are an indicator of continental organic matter or immature organic matter from all sources. Ol = (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

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 x 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/CO₂ detectors
- Combustion with gas separation and FID (pedestal, oven, and conversion FID)



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 | ТРН |
| OTHR2765092 | OTHR130746 | 92.36 | 4 | UNK | ТРН |
| | | | | | |
| | | | | | |
| CV2-99986 | OTHR427034 | 92.05 | 10 | QAQCCV | ТРН |

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

| | General Data & Report Pedestal AS Tray Temps Factory IN |
|---|--|
| A BAR ST | Pre-Run check Individual Sample Report Sequence Report Wait for Equilibrium FID Printer Printer Place a cost MD MD FID |
| | Zere |
| INSTRUMENTS DIVISION | CSV File Creation |
| | 611 CSV Data Rows |
| Configuration Method Editor About | Save Data & Report Settings |
| Preview Sequence Editor Acquisition | |
| | |
| ath : C:\Program Files (x86)\Thermal Station\Data\371_NSTRUMENTTEST_VP re 3: Acquisition software main screen ration ration upgral Data & Report Perfectal ASTray Tempel Factor IN | |
| ath : C:\Program Files (x86) Thermal Station\Data\371_NSTRUMENTTEST_VP re 3: Acquisition software main screen ration neral Data & Report Pedestal AS Tray Temps Factory INI veration Temperature Settings Oven Standby Temperature 300 Detector (FID) Standby Temperature 000 | Configuration Figure 4: Data and Report tab of the Configuration Menu Configuration General Data & Report Pedestal AS Tray Temps Factory II General Settings Instrument name SFA Data Path C:VProgram Files (x86)/Thermal Station/Data/371_INSTRUMENTTEST_VP Analysis Type TPH TOC (\$1, \$2, \$3, Tmax, TOC, H, |
| ath : C:VProgram Files (x86)\Thermal Station\Data\371_NSTRUMENTTEST_VP ref 3: Acquisition software main screen ration meral Data & Report Pedestal AS Tray Temps Factory INI peration Temperature Settings Oven Standby Temperature Detector (FID) Standby Temperature Detector (FID) Standby Temperature 0.00 Send Temperatures Immediately | Configuration Figure 4: Data and Report tab of the Configuration Menu Configuration General Data & Report Pedestal AS Tray Temps Factory General Settings Instrument name SRA Data Path C:VPogram Files (x88))Thermal Station/Data/371_INSTRUMENTTEST_VP Analysis Type TFH TOC (\$1, 52, 53, Tmax, TOC, H, O) Gas Settings Carrier gas Carrier Diverter OAir @He Vent Gases always ON |
| sh : C:\Program Files (x86))Thermal Station/Data\371_INSTRUMENTTEST_VP re 3: Acquisition software main screen ration neral Data & Report Pedestal AS Tray [Temps] Factory INI reration Temperature Settings Oven Standby Temperature Detector (FID) Standby Temperature 325 0.00 Send Temperature Send Temperature Send Temperature Send Temperature Save Temp Settings | Configuration Figure 4: Data and Report tab of the Configuration Menu Configuration General Data & Report Pedestal AS Tray Temps Factory General Settings Instrument name SRA Data Path C:Program Files (x86)/Thermal Station/Data/371_INSTRUMENTTEST_VP Analysis Type TFH TOC (\$1, 52, 53, Timax, TOC, H, OI) Gas Settings Carrier gas Carrier Diverter OI Gas satings Carrier gas Carrier Diverter OI Gas satings Carrier Carrier Diverter OI Gas Satings Carrier Carrier Diverter OI Gas Satings Carrier Carr |

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 H₂, 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.
- Zero and calibrate the CO/CO₂ 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 10: IR Calibration screen

Figure 9: Setup of the IR cell calibration

Setting up the Software Prepare the software for data acquisition as follows:

- ٠ Create a data folder
- Edit the method (if needed) Edit the sequence table ٠
- •

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*).

| ethod file: SRA.sram | ~ | Method file: SRA.sram | ~ `` |
|--|--|--|---|
| Pyrolysis Initial Temp (°C) 300 Initial Time (Min) 3 Rate (°C/Min) 25. Final Temp (°C) 600 Final Time (Min) 1 Slicing Start (mm:ss) - Stop (mm:ss | emp (°C) 325 dation urge (Min) 5 ime (Min) 20 emp (°C) 580) End of Run | Calibrated IR Baseline: | vOCC(S3) 1.37 S4 29.3 -11.93024° 1.353165E+08 4.99mV S3: 4.09E+8 S4: 9.49E+8 CO2 (Pyrolysis): 49.02mV CO2 (Oxidation): 50.51mV CO: 46.14mV |
| FID Gain © Low (10^6) Mid (10^7) High (10^8) Aproximated Run Time: 0h 43m | 120 | STD Calibrated DateTime : BLK Calibrated DateTime : | 7/18/2017 8:58:44 AM 7/18/2017 8:02:48 AM |
| Print | Save As Llose | | Print Save As Llose |

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

| Sequence Editor (371_InstrumentTest_VP.sras) | | | | | | | | | | | | | | | | | |
|--|---|-----------------------------|------|-----------|--------------------|------------------|----------|-----------|-------|------------|------------------------|----------------|-------------------------|--------|----------------|----------|------|
| Sequence File: | equence File: 371_InstrumentTest_VP.sras | | | | | | | | | | | | | | | | |
| Comments: | This tested the SRA V2 with new pc and Windows 10 software. New IStationAcg program as well. | | | | | | | | | | | | | | | | |
| Approximate To Entire Row Append | tal Sequence Run Time: 6 Insert Delete | h 24m Individual Copy | Cell | Paste | | | | | | | | | | | | | |
| Data File | Sample ID | Method | C# | Lithology | Lithology Other | Sample Weight | Acq Type | Well Name | Depth | Depth Type | Depth Type Other | Sample Type | Sample Type Other | Job ID | Depth Units | | |
| 1 BLK | Blank | SRA | 1 | | | 0.0 | BLK | | | | | | | | | | |
| 2 STD | 371T_STD533 | SRA | 2 | | | 99.1 | STD | | | | | | | | | | |
| 3 STDCHK1 | 371T_CHK533_1 | SRA | 3 | | | 100.1 | TPH | | | | | | | | | | |
| 4 STDCHK2 | 371T_CHK533_2 | SRA | 4 | | | 98.3 | TPH | | | | | | | | | | |
| 5 STDCHK3 | 371T_CHK533_3 | SRA | 5 | | | 100.1 | TPH | | | | | | | | | | |
| 6 STDCHK4 | 371T_CHK533_4 | SRA | 6 | | | 99.2 | TPH | | | | | | | | | | |
| 7 STDCHK5 | 371T_CHK533_5 | SKA | | | | 101.7 | TPH | | | | | | | | | | |
| 8 STDCHK6 | 371T_CHK533_6 | SRA | 8 | | | 99.4 | TPH | | | | | | | | | | |
| New | Import | | | | | | | | | | | | | P | rint S | ave As C | lose |

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.

| Acquisition | March 10C - Acq Type: TPH - 25°C/min (v7.0.4) - X |
|--|--|
| File | Status Start Sequence Bypass Analysis Abort Sequence Close |
| Operator percuoco | Running Acquiring |
| Acquisition Sequence: 371_INSTRUMENTTEST_VP.SRAS Sequence Crucible DataFile Salection All 02 2 STD All 03 3 STDCHK1 04 4 STDCHK2 8 of 8 05 5 STDCHK3 v Data Folder 371_InstrumentTest_VP C:\Program Files (x86) C:\Vindows] v C:\Vindows] v C | FD Signal 5.39mV FD Temp 325* C02 Signal 259.23mV C0 Signal 58.91mV 58.91mV Sample Temp 578* FID Scale C02 / C0 Scale Plot Real-Time Data \$ Auto C02 / C0 Scale Plot Real-Time Data \$ Auto \$ Auto C02 / C0 Scale Plot Real-Time Data \$ Auto \$ C0 Signal |
| Next > Cancel | Sequence C:\Program Files (x86)\Ther\371_InstrumentTest_VP.sras View Method C:\Program Files (x86)\Thermal Station\Methods\SRA.sram View |
| Figure 14. SRA > Acquisition. | Data File C:\Program Files (x86)\Thermal1_INSTRUMENTTEST_VP\STDCHK4.RAW Crucible Number (C#) 6 Current Sequence Line 1 of 3 Acquisition Type [TPH] Method Information 300° Initial Iso Time 3 Sample Information Initial Temp 300° Total Run Time 43.0 Sample Information ID 371T_CHK533_4 FID Temp 325° Gain Low(10°6) Weight 99.2 Purge Time (secs)[120 Weight 99.2 Weight 99.2 Dadation |

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.

| STDCHK2.RAW - TPH TOC Analysis - X | STDCHK2.RAW - Details |
|--|---|
| Hie Edit View Help | Gample Information |
| | Acquisition Date: July 18 2017, 10:08:38 AM |
| | Sequence File: C:\Program Files (x86)\Thermal Station\Sequence\371_InstrumentTest_VP. |
| 66.26mV | Method File: C:\Program Files (x86)\Thermal Station\Methods\SRA.sram |
| IR CO 941.07mV | Crucible: 4 Well Name: |
| | SampleID: 371T_CHK533_2 Depth: |
| 941.07mV | Lithology: Depth Type: |
| | Weight: 98.3 Sample Type: |
| | Acquisition Type: TPH Instrument Name: SRA |
| | Method Information |
| | Oven Oxidation |
| | Purge Time (secs): 120 Time (Min): 20 |
| 5:00 10:00 15:00 20:00 25:00 30:00 35:00 40:00 | Initial Temp (°C): 300 Temp (°C): 500 |
| Results | Initial Time (Min): 3 |
| VTPH (S1): 0.48 mg/g [pTPH (S2): 12.67 mg/g [cTemp(Tmax): 418.8 °C [tTemp: 457.8 °C S3: 1.26 mg/g [TOC: 3.96 % | Rate (°C/Min): 25.00 STD Parameters |
| HI: 320 JUI: 32 JPI: 0.04 IST/TUC: 0.12 | Final Temp (°C): 600 tTemp (°C): 458.00 |
| Salipelo. 311_CHK335_2 Pie. STOCHA2.haw | Final Time (Min): 1 |
| iguro 16: TStationBros program monu with cample row file | Total Time (Min): 43.00 S3 mg/g: 137 |
| ngure to. Totation roc program menu with sample raw me | FID S4 ma/a: 29.3 |
| Jaded | Temp (°C): 325 |
| | Gain: Low (10 ⁶) |
| | Comments: |
| | Galibration Responses |
| | BLK Response STD Temp Offset: -11.93 |
| | FID: 4.99mV STD Response |
| | IR CO2 (pyrolysis): 49.02mV FID S2: 1.35E+8 |
| | IR CO2 (oxidation): 50.51mV IR S3 (CO2): 4.09E+8 |
| | IR CO: 46.14mV IR S4 (CO+CO2): 9.49E+8 |
| | Calib Date: 7/18/2017 8:02:48 AM Calib Date: 7/18/2017 8:58:44 AM |
| | Show ToofTips Print |
| | 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 | н | 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

- ٠
- 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.

LIMS Component Table

Although there's a component list in the LIMS Integration section, it is not all of the components either created by the LIMS or the uploader. The list below describes all of them.

| AN AL YSIS | TAB LE | NAME | ABOUT TEXT |
|------------------|------------|------------------------|---|
| SR ANL | SAM PLE | Exp | Exp: expedition number |
| SR ANL | SAM PLE | Site | Site: site number |
| SR ANL | SAM PLE | Hole | Hole: hole number |
| SR ANL | SAM PLE | Core | Core: core number |
| SR ANL | SAM PLE | Туре | Type: type indicates the coring tool used to recover the core (typical types are F, H, R, X). |
| SR ANL | SAM PLE | Sect | Sect: section number |
| SR ANL | SAM PLE | A/W | A/W: archive (A) or working (W) section half. |
| SR ANL | SAM PLE | text_id | Text_ID: automatically generated database identifier for a sample, also carried on the printed labels. This identifier is guaranteed to be unique across all samples. |
| SR ANL | SAM PLE | sample_n umber | Sample Number: automatically generated database identifier for a sample. This is the primary key of the SAMPLE table. |
| SR ANL | SAM PLE | label_id | Label identifier: automatically generated, human readable name for a sample that is printed on labels. This name is not guaranteed unique across all samples. |
| SR ANL | SAM PLE | sample_n ame | Sample name: short name that may be specified for a sample. You can use an advanced filter to narrow your search by this parameter. |
| SR ANL | SAM PLE | x_sample _state | Sample state: Single-character identifier always set to "W" for samples; standards can vary. |
| SR ANL | SAM PLE | x_project | Project: similar in scope to the expedition number, the difference being that the project is the current cruise, whereas expedition could refer to material/results obtained on previous cruises |
| SR ANL | SAM PLE | x_capt_loc | Captured location: "captured location," this field is usually null and is unnecessary because any sample captured on the JR has a sample_number ending in 1, and GCR ending in 2 |
| SR ANL | SAM PLE | location | Location: location that sample was taken; this field is usually null and is unnecessary because any sample captured on the JR has a sample_number ending in 1, and GCR ending in 2 |
| SR ANL | SAM PLE | x_sampli ng_tool | Sampling tool: sampling tool used to take the sample (e.g., syringe, spatula) |
| SR ANL | SAM PLE | changed_ by | Changed by: username of account used to make a change to a sample record |
| SR ANL | SAM PLE | changed_ on | Changed on: date/time stamp for change made to a sample record |
| SR ANL | SAM PLE | sample_t ype | Sample type: type of sample from a predefined list (e.g., HOLE, CORE, LIQ) |
| SR ANL | SAM PLE | x_offset | Offset (m): top offset of sample from top of parent sample, expressed in meters. |
| SR ANL | SAM PLE | x_offset_ cm | Offset (cm): top offset of sample from top of parent sample, expressed in centimeters. This is a calculated field (offset, converted to cm) |
| SR ANL | SAM PLE | x_bottom _offset_cm | Bottom offset (cm): bottom offset of sample from top of parent sample, expressed in centimeters. This is a calculated field (offset + length, converted to cm) |
| SR ANL | SAM PLE | x_diamet er | Diameter (cm): diameter of sample, usually applied only to CORE, SECT, SHLF, and WRND samples; however this field is null on both Exp. 390 and 393, so it is no longer populated by Sample Master |

| SR ANL | SAM PLE | x_orig_len | Original length (m): field for the original length of a sample; not always (or reliably) populated |
|-----------|--------------------|---------------------------------|---|
| SR ANL | SAM PLE | x_length | Length (m): field for the length of a sample [as entered upon creation] |
| SR ANL | SAM PLE | x_length_ cm | Length (cm): field for the length of a sample. This is a calculated field (length, converted to cm). |
| SR ANL | SAM PLE | status | Status: single-character code for the current status of a sample (e.g., active, canceled) |
| SR ANL | SAM PLE | old_status | Old status: single-character code for the previous status of a sample; used by the LIME program to restore a canceled sample |
| SR ANL | SAM PLE | original_s ample | Original sample: field tying a sample below the CORE level to its parent HOLE sample |
| SR ANL | SAM PLE | parent_sa mple | Parent sample: the sample from which this sample was taken (e.g., for PWDR samples, this might be a SHLF or possibly another PWDR) |
| SR ANL | SAM PLE | standard | Standard: T/F field to differentiate between samples (standard=F) and QAQC standards (standard=T) |
| SR ANL | SAM PLE | login_by | Login by: username of account used to create the sample (can be the LIMS itself [e.g., SHLFs created when a SECT is created]) |
| SR ANL | SAM PLE | login_date | Login date: creation date of the sample |
| SR ANL | SAM PLE | legacy | Legacy flag: T/F indicator for when a sample is from a previous expedition and is locked/uneditable on this expedition |
| SR ANL | TEST | test changed_ on | TEST changed on: date/time stamp for a change to a test record. |
| SR ANL | TEST | test status | TEST status: single-character code for the current status of a test (e.g., active, in process, canceled) |
| SR ANL | TEST | test old_status | TEST old status: single-character code for the previous status of a test; used by the LIME program to restore a canceled test |
| SR ANL | TEST | test test_num ber | TEST test number: automatically generated database identifier for a test record. This is the primary key of the TEST table. |
| SR ANL | TEST | test date_rece ived | TEST date received: date/time stamp for the creation of the test record. |
| SR ANL | TEST | test instrument | TEST instrument [instrument group]: field that describes the instrument group (most often this applies to loggers with multiple sensors); often obscure (e.g., user_input) |
| SR ANL | TEST | test analysis | TEST analysis: analysis code associated with this test (foreign key to the ANALYSIS table) |
| SR ANL | TEST | test x_project | TEST project: similar in scope to the expedition number, the difference being that the project is the current cruise, whereas expedition could refer to material/results obtained on previous cruises |
| SR ANL | TEST | test sample_n umber | TEST sample number: the sample_number of the sample to which this test record is attached; a foreign key to the SAMPLE table |
| SR ANL | CAL CUL ATED | Top depth CSF-A (m) | Top depth CSF-A (m): position of observation expressed relative to the top of the hole. |
| SR ANL | CAL CUL ATED | Bottom depth CSF-A (m) | Bottom depth CSF-A (m): position of observation expressed relative to the top of the hole. |
| SR ANL | CAL CUL ATED | Top depth CSF-B (m) | Top depth [other] (m): position of observation expressed relative to the top of the hole. The location is presented in a scale selected by the science party or the report user. |
| SR ANL | CAL CUL ATED | Bottom depth CSF-B (m) | Bottom depth [other] (m): position of observation expressed relative to the top of the hole. The location is presented in a scale selected by the science party or the report user. |
| SR ANL | RES ULT | н | RESULT hydrogen index (HI): normalized hydrocarbon content of a rock sample (S2 x 100/TOC); HI decreases as the hydrocarbons in the sample mature. Range is generally ~100-600. |
| SR ANL | RES ULT | OI | RESULT oxygen index (OI): normalized oxygen content of a rock sample (S3 x 100/TOC). High OI values (>100) indicate continental or immature organic matter. |

| SR | RES | PC (mg | RESULT pyrolysis carbon (PC, mg/g): represents carbon content of free hydrocarbons generated plus the carbon content of the remaining potential hydrocarbons ([0.83 x (S1 + S2)/10]. |
|-----------|------------|--------------------------|---|
| ANL | ULT | /g) | |
| SR ANL | RES ULT | PI | RESULT production index (PI): indicates conversion of kerogen into free hydrocarbons and increases with increasing thermal maturation ([S1/(S1 + S2)] x 100). |
| SR | RES | S1 (mg | RESULT S1 (mg HC/g C): indicates quantity of free hydrocarbons (gas and oil) in the sample and normally increases with depth. Units are milligrams of hydrocarbon per gram of rock; multiply by 1000 to convert to ppm. |
| ANL | ULT | HC/g C) | |
| SR ANL | RES ULT | S2 (mg HC/g C) | RESULT S2 (mg HC/g C): indicates quantity of hydrocarbons that the rock has the potential of producing if burial and maturation continue and normally decreases with burial depths >1 km (also referred to as kerogen). Units are milligrams of hydrocarbon per gram of rock; multiply by 1000 to convert to ppm. |
| SR | RES | S3 (mg | RESULT S3 (mg HC/g C): indicates the amount of oxygen in the kerogen evolved as carbon dioxide during pyrolysis. Units are milligrams of organic carbon dioxide per gram of rock. |
| ANL | ULT | HC/g C) | |
| SR | RES | container | RESULT container number: number of the container/autosampler position for this sample |
| ANL | ULT | _number | |
| SR | RES | csv_asm | RESULT csv file ASMAN_ID: serial number of ASMAN record for the CSV data file |
| ANL | ULT | an_id | |
| SR | RES | csv_filena | RESULT spreadsheet uploader filename: file name of the CSV data file |
| ANL | ULT | me | |
| SR | RES | pdf_asma | RESULT image file ASMAN_ID: serial number of ASMAN record for the image file (for the thermogram); may be in PDF, PNG, or other image format |
| ANL | ULT | n_id | |
| SR | RES | pdf_filena | RESULT image filename: file name of the image file (for the thermogram); may be in PDF, PNG, or other image format |
| ANL | ULT | me | |
| SR | RES | raw_asm | RESULT raw data ASMAN_ID: serial number of ASMAN record for the raw data file (binary format) |
| ANL | ULT | an_id | |
| SR | RES | raw_filen | RESULT raw data filename: file name of the raw data file (binary format) |
| ANL | ULT | ame | |
| SR | RES | sr_mass | RESULT sample mass (mg): mass of the sample for this run |
| ANL | ULT | (mg) | |
| SR | RES | ssup_as | RESULT spreadsheet uploader ASMAN_ID: serial number of ASMAN record for the spreadsheet uploader file |
| ANL | ULT | man_id | |
| SR | RES | ssup_file | RESULT spreadsheet uploader filename: file name of spreadsheet uploader file |
| ANL | ULT | name | |
| SR ANL | RES ULT | tmax (°C) | RESULT Tmax (deg. C): indicates the stage of maturation of the organic matter. It is determined by the temperature at the maximum S2 yield. Units are degrees Celcius, and the range is generally 400°-550°C. |
| SR ANL | RES ULT | toc (wt%) | RESULT total organic carbon (TOC, wt%): TOC represents the convertible carbon fraction (pyrolized carbon + residual carbon). Units are unit weight of carbon per unit weight of whole rock (wt%). |
| SR | SAM | sample | SAMPLE comment: contents of the SAMPLE.description field, usually shown on reports as "Sample comments" |
| ANL | PLE | description | |
| SR ANL | TEST | test test_com ment | TEST comment: contents of the TEST.comment field, usually shown on reports as "Test comments" |
| SR | RES | result | RESULT comment: contents of a result parameter with name = "comment," usually shown on reports as "Result comments" |
| ANL | ULT | comments | |

Archive Versions

LMUG-SRAUserGuide-230220-1922-168.pdf