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v.378P

FlashEA 1112 Elemental Analyzer (CHNS): User Guide

Manual Information

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Management Approval:	D.J. Houpt, Supervisor of Analytical Systems		
Audience:	Laboratory/Research Specialists, Scientists		
Origination Date:	5/6/08		
Current Version:	Final 4/30/10	Version 1.0	
Revised:	Version 1.21	71/13/14 15 (IODP-II)V371T	July 2017
Domain:	Chemistry		

System:	CHNS Elemental Analysis
Keywords:	Carbon, nitrogen, hydrogen, sulfur

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Introduction

Carbon, hydrogen, nitrogen, and sulfur (CHNS) are fundamental elemental components that are analyzed on the ship during IODP expeditions. Fluctuations in the concentration and/or content ratio of carbon, nitrogen, and sulfur define the origin, depositional environment, and diagenetic alteration of source materials. A few options for sample preparation method, instrument settings, and measurement methodology exist. In addition to the pregenerated methods, specific analytical methodology may be required based on the nature of certain sample materials. In this case, new methods will be created by the laboratory technicians working in conjunction with the scientists. Each instrument method is recorded by the USIO and will be associated with the measurements performed under that method.

Carbon Analysis

Most marine sediments and sedimentary rocks contain both carbonate ("inorganic") carbon and organic carbon. The CHNS procedure measures total carbon (inorganic plus organic) when following the standard method. Organic carbon content is then determined by using the inorganic carbon value from coulometric analysis and calculating the difference between total carbon from CHNS analysis and inorganic carbon analyzed by coulometer. Alternative methodologies can be employed to measure organic and inorganic carbon.

Nitrogen Analysis

Nitrogen is one of the important limiting nutrients in the ocean. The global carbon cycle and, consequently, atmospheric CO₂ might be tightly coupled to the nitrogen cycle, and therefore changes in the magnitude of the sinks and sources of fixed nitrogen in the oceans can significantly influence global climate. Biological nitrogen fixation, denitrification, and consumption of nitrate by phytoplankton are the major biological processes of the global nitrogen cycle. Changes in ocean circulation and nutrient supply, which occur in response to changes in environmental conditions, affect the relative importance and spatial extent of the major pathways of the nitrogen cycle.

Carbon-Nitrogen Relationship

C-N signatures indicate diagenesis and changes in productivity in seafloor sediments. Diagenesis may cause a decrease in C/N with decoupled C-N concentration variations, whereas productivity changes tend to produce C-N covariance in concentrations at relatively constant C/N ratios. Without significant superimposed diagenetic effects, linear relationships between C and N compositions can in some cases be interpreted as reflecting sources of organic matter:

- C/N = 6–8: fresh marine organic matter
- C/N = 8–20: degraded marine organic matter
- C/N > 20: continental organic matter

Low C/N values occur in sediment that is poor in organic carbon; these values may be biased by the tendency of clay minerals to absorb ammonium ions generated during the degradation of organic matter. Sediments rich in TOC have higher C/N values than sediments lean in TOC. C/N values that are elevated above algal values are common in organic carbon-rich marine sediments. These values evidently result from the selective loss of nitrogen as organic matter settles from the photic zone because nitrogen-bearing proteins are more labile than other organic matter components such as carbohydrates and lipids. This type of preferential nitrogen depletion and consequent carbon enrichment is recognized in organic carbon-rich sediments. C/N elevations are most pronounced when TOC concentrations are highest, suggesting that a higher rate of organic matter delivery leads to diminished organic matter degradation.

Sulfur Analysis

Cycling of sulfur compounds is a ubiquitous process in marine sediments that supports a range of microbial metabolic strategies. The occurrence of sulfur over a wide range of oxidation states (-2 to +6) allows sulfur species to serve as both electron acceptors and electron donors. In reduced form as sulfide ($\text{H}_2\text{S} = \text{H}_2\text{S}_{(\text{aq})} + \text{HS}^-$), sulfur is also an important sink for reactive iron. The reduction of sulfate to sulfide is by far the most important pathway for sedimentary organic matter oxidation in anoxic marine sediments, and there is evidence that anaerobic oxidation of methane controls microbial sulfate reduction (MSR) in many marine systems.

Much of the sulfide produced during dissimilatory MSR in marine sediments is oxidized back to sulfate by a variety of biological and abiotic pathways, and sulfate produced by oxidation of sulfide may have variable isotope values reflecting the nature and complexity of the abiotic and biological oxidation pathways and relative contributions from different oxidants. These pathways often include the production of intermediate sulfur species such as elemental sulfur and thiosulfate, which can undergo further bacterial disproportionation reactions that may lead to further fractionations of both sulfur and oxygen isotopes in secondary sulfate.

Elemental sulfur is a possible intermediate in pyrite formation and may serve as an indicator for active SO_4^{2-} reduction. Elemental sulfur enrichments may form at places where the sulfide concentrations were high, resulting from in situ SO_4^{2-} reduction. Elemental sulfur forms from partial oxidation of sulfide. In addition, low-molecular-weight organic sulfur compounds are included in elemental sulfur.

Sulfur-Carbon Relationship

In normal marine sediments the relation between sulfur and carbon contents has a slope of 1/2.8 ($\text{S}_{\text{tot}}/\text{C}_{\text{org}}$ ratio, wt%/wt%) and passes through the origin (assuming that sulfur fractions other than reduced sulfur are relatively negligible). In euxinic marine environments, however, sulfide is omnipresent (independent of local C_{org} contents) and iron sulfide formation can take place in the water column or at the sediment/water interface.

In addition, even slowly reacting iron compounds may react with sulfide in euxinic environments. Consequently, positive intercepts on the sulfur axis are obtained in sulfur vs. carbon plots for euxinic sediments, and only weak correlations may be observed. Additionally, post-depositional sulfidization of C_{org} -poor sediments may result in extremely high sulfur/carbon ratios.

Theory of Operation

Dried and powdered samples are combusted in a tin sample crucible with vanadium pentoxide catalyst, purified by a reactor packed with electrolytic copper and copper oxide, separated on a gas chromatographic column, and analyzed using a thermal conductivity detector (TCD). Addition of the V_2O_5 ensures complete conversion of inorganic sulfur in the sample to sulfur dioxide.

When the tin crucible with sample is dropped into the reactor, the oxygen environment triggers a strong exothermic reaction. Temperature rises to 1800°

C, causing the sample to combust. The combustion products are conveyed across the reactor, where oxidation is completed. Nitrogen oxides and sulfur trioxide are reduced to elemental nitrogen and sulfur dioxide and oxygen excess is retained. The gas mixture containing N_2 , CO_2 , H_2O , and SO_2 flows into the chromatographic column, where separation takes place. Eluted gases are sent to the TCD where electrical signals processed by the *Eager 300* software provide percentages of nitrogen, carbon, hydrogen, and sulfur contained in the sample.

Apparatus, Reagents, & Materials

Hardware

Carbon, hydrogen, nitrogen, and sulfur are analyzed on a Thermo Electron Corporation FlashEA 1112 CHNS elemental analyzer (*Figure 1*) with autosampler (*Figure 2*).

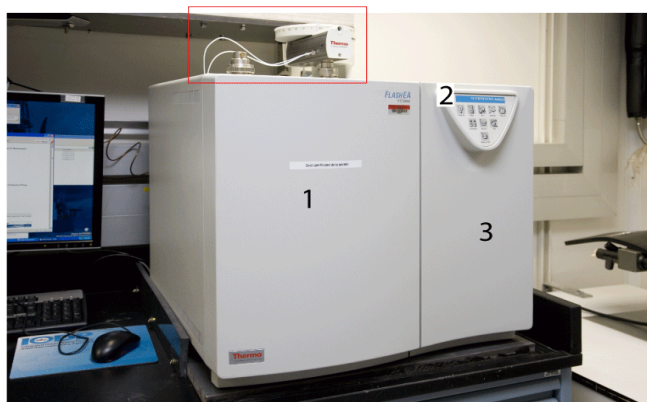


Figure 1. Elemental Analyzer: (1) Furnace Access Door, (2) Synoptic Panel, and (3) Thermostatic Chamber Access. Dry Sample Autosampler is located on top of furnace.

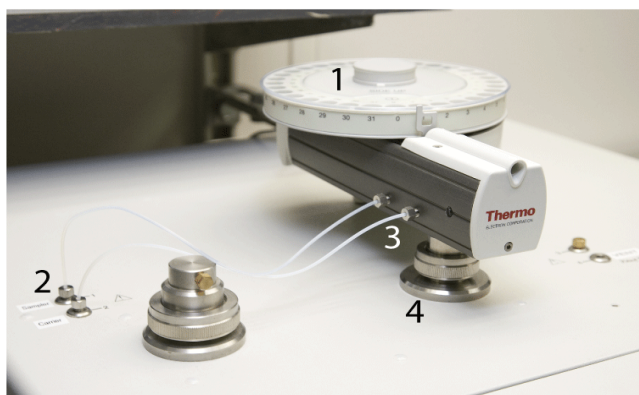


Figure 2. Dry Sample Autosampler (red box in Figure 1): (1) Drum, (2) Gas Connection Fitting, (3) Gas Tube, and (4) Reactor Fitting..

Laboratory Apparatus

- Agate mortar and pestle: well washed and dried
- Chamber for freeze drier: well washed and dried
- Dessicator and silica gel: use activated and well-dried silica gel
- Medical paper
- Mill (for hard rock samples)
- Kimwipes
- Sample holder: stainless steel with 50 numbered holes
- Spatula
- Spatula (general laboratory spoon): stainless steel, well washed and dried
- Spring tweezers (2)
- Tin containers (set of 100): Thermo Electron PN 240 064 00

Chemicals and Reagents

Be sure to read the Health, Safety, and Environment section before using any of the chemicals and reagents in this method.

Gases

- Helium (carrier gas): chromatography grade
- Oxygen (sample oxidation gas): 99.995% minimum purity

Reagents

Note that many of these materials are hazardous and before any work is done with them, the user must be familiar with the appropriate Material Safety Data Sheets (MSDS).

Material Name	Description	Purpose
Aspartic acid	$C_4H_7NO_4$: white fine crystals	Standard reference material
2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene (BBOT)	$C_{26}H_{26}N_2O_2S$: pale green crystals	Standard reference material
Copper oxide	Pre-packed	Filling material
Electrolytic copper	Pre-packed	Filling material
Ethanol	C_2H_5OH	Solvent for sample preparation
Quartz wool	SiO_2	Filling material
Soil Reference Material	Light brown powder	Reference for N and C
Sulfanilamide	$C_6H_8N_2SO_2$: white odorless crystals	Calibration standard for CHNS and CNS
L-Cystine	$C_6H_{12}N_2O_4S_2$: white odorless crystals	Calibration standard
Vanadium pentoxide	V_2O_5 : yellow to red crystalline powder	Catalyst
Magnesium perchlorate	$Mg(ClO_4)_2$: white granulate	Filling material for water trap

Sample Preparation

Bulk samples are freeze-dried, crushed and homogenized using a mortar and pestle or electric mill, and weighed into a tin sample cup (crucible) with vanadium pentoxide catalyst. The crucibles are then closed (referred to as "wrapping" the sample) and placed in the autosampler for instrumental analysis.

Drying and Homogenizing the Sample

1. Break clumpy sample into pieces.
2. Fill a freeze-drying chamber with sample pieces and place into freeze dryer.
3. Freeze-dry sample for at least 12 hr until sample is completely dry (may require additional freeze-drying time, up to 3 hr). The sample is dry when there is no more condensate in the cold part of the tube.
4. Note: do not overload the freeze dryer; it will not dry properly.
5. Wipe an agate mortar and pestle with ethanol and allow to dry completely before grinding each sample. Be sure the mortar and pestle are *completely* dry; ethanol reagent residue can cause false C and H results.
6. Grind and homogenize sediment using the cleaned *and dry* agate mortar and pestle.
7. Fill a sample bottle with powdered homogenized sediment.
8. Place sample bottle into the desiccator. Many mineral species are hygroscopic (tend to absorb water), so the sample bottles containing the dried samples should be kept in the desiccator until used.

Sample Volume

Because the balance system is of unknown lower precision aboard ship than in a shore-based laboratory, we recommend 6–9 calibration points to obtain a high CHNS measurement precision. The usual quantities of sample materials and standards used are as follows:

–Vanadium pentoxide: ½ of small spatula for blank, standard, and unknown samples

–Standard (sulfanilamide):

- 3.0 mg × 2 to 3 replicates
- 5.0 mg × 2 to 3 replicates
- 7.0 mg × 2 to 3 replicates
- Note: Sulfanilamide is not necessarily the right standard for a given set of samples: try to bracket your unknown samples with the standards for each element of interest.

–Standard sediment or sulfanilamide (for QA/QC evaluation; see *Quality Assurance/Quality Control*): 11 mg, minimum 10 pieces may be required for one sequence of the measurement.

–Unknown samples: The amount used depends on the nature of the sample material. If material is unusual, it may be necessary to weigh out several different quantities of sample to correctly analyze the material. Typical masses of some materials are:

- Hemipelagic sediments: 11–12 mg
- Pelagic sediments (low productivity): 11–15 mg
- Upwelling area (high productivity area): 10–12 mg

Clean Preparation Equipment

Wipe spatula, spring tweezers, balance, and other stainless equipment with ethanol between each sample. *Be sure these are completely dry before using to avoid contaminating samples.*

Weighing and Wrapping Samples

1. Double-click the **Cahn Balance** icon.
2. Log into the system by entering LIMS user name and password.
3. Enter 200 as the Count Limit.
4. Place an empty crucible (tin container) on the REFERENCE balance pan (right pan).
5. Place a new crucible into the small hole of the metal plate.
6. Open the upper half of the tin cup and place a crucible on the UNKNOWN balance pan (left pan).
7. Tare the balance using the software. (Do **not** press the Tare button on the Cahn balance.)
8. Click **Start** to start weighing.
9. Once the mass volume is acceptable, click **Get Mass**.
10. Remove the crucible from the UNKNOWN balance pan, place the crucible on the metal plate, and place the appropriate amount of sample material (see *Sample Volume*) into the crucible.

NOTE: DO NOT use the holes on the metal plate if any standard material is spilled in or near it because even a small amount of standard may contaminate the measurement.

1. Place crucible with sample material back on the UNKNOWN balance pan and close door.
2. Click **Weigh** and **Start**.
3. Click **Get Mass** if the mass value is acceptable.
4. Enter any part of a sample ID or Label ID and click **Search**.
5. Select the sample that was just weighed from the list and click **Assign**.
6. Enter a container number (sample holder number, not an autosampler number) in the *Container#* field.
7. Click **Save**.

Sample Analysis

Data flow for CHNS sample analysis includes the following:

- Prepare the instrument for running samples (see *Preparing the Instrument*).
- Confirm instrument calibration (see *Verifying Instrument Calibration*).
- Export LIMS file from LabWare for CHNS (see *Creating the Sample Table*).
- Import LIMS sample table and edit (see *Uploading the Sample Table to Eager 300 Software*).
- Start sequence (see *Running Samples*).
- Summarize, edit, and analyze results (see *Analyzing Data*).
- Export sample data as CSV file and upload to LIMS (see *LIMS Integration*).

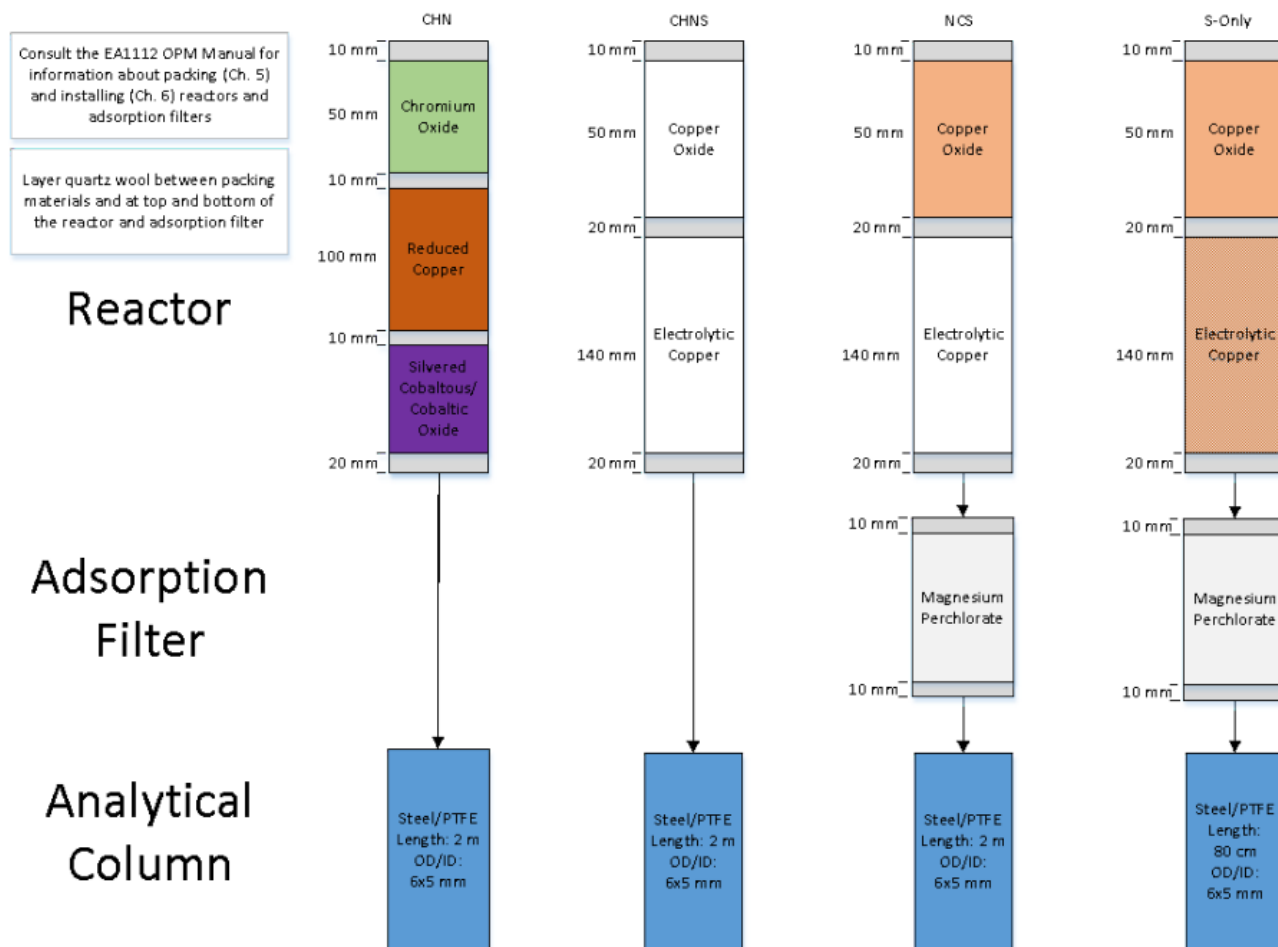
Preparing the Instrument

The shipboard technician will set up and maintain the reactor and gas chromatographic column. The technician will also instruct the scientist on the operation of the instrument.

Instrument startup and conditioning are conducted by the shipboard technician, who also loads the analytical configuration (method). If a specific analytical configuration is required because of the nature of the samples, scientists should collaborate with the technician to develop the analytical method and run parameters. When the instrument is ready, the *Eager 300 CHNS* screen displays. To confirm the status of the CHNS analyzer instrument, select **View > View Elemental Analyzer Status** (see Figure 4, below). (Figure 3). Analytical determination takes approximately 40, 100, 150, and 640 seconds for nitrogen, carbon, hydrogen and sulfur, respectively, for a 2 m long separation column. The integration time should be set to approximately 15 min (900 sec) for runs in which sulfur is measured due to the breadth of the signal peak. Either purchase pre-filled reactor columns or prepare them according to the manufacturer's instructions. The adsorption filter should be filled with fresh magnesium persulfate regularly. The JRSO uses pre-packed reactor columns from CE Elantech and Costech; these have always proved to be of high quality, without gaps or faults in the reagents that could lead to a poorly-reacted gas stream.

If pre-filled reactor columns are not available, follow the instructions in the Flash EA 1112 vendor manual to prepare them. Packing columns is in Chapter 5 of the vendor manual; installing reactor and adsorption columns is discussed in Chapter 6. Note that the JRSO uses CE Elantech 061110 columns for sulfur, loaded with copper and tungsten oxide, but many other options are possible.

A general schematic is shown below in Figure 3. Prepare the EA reactor, adsorption filter, and chromatographic column for the desired analytical elements according to the following schematic:



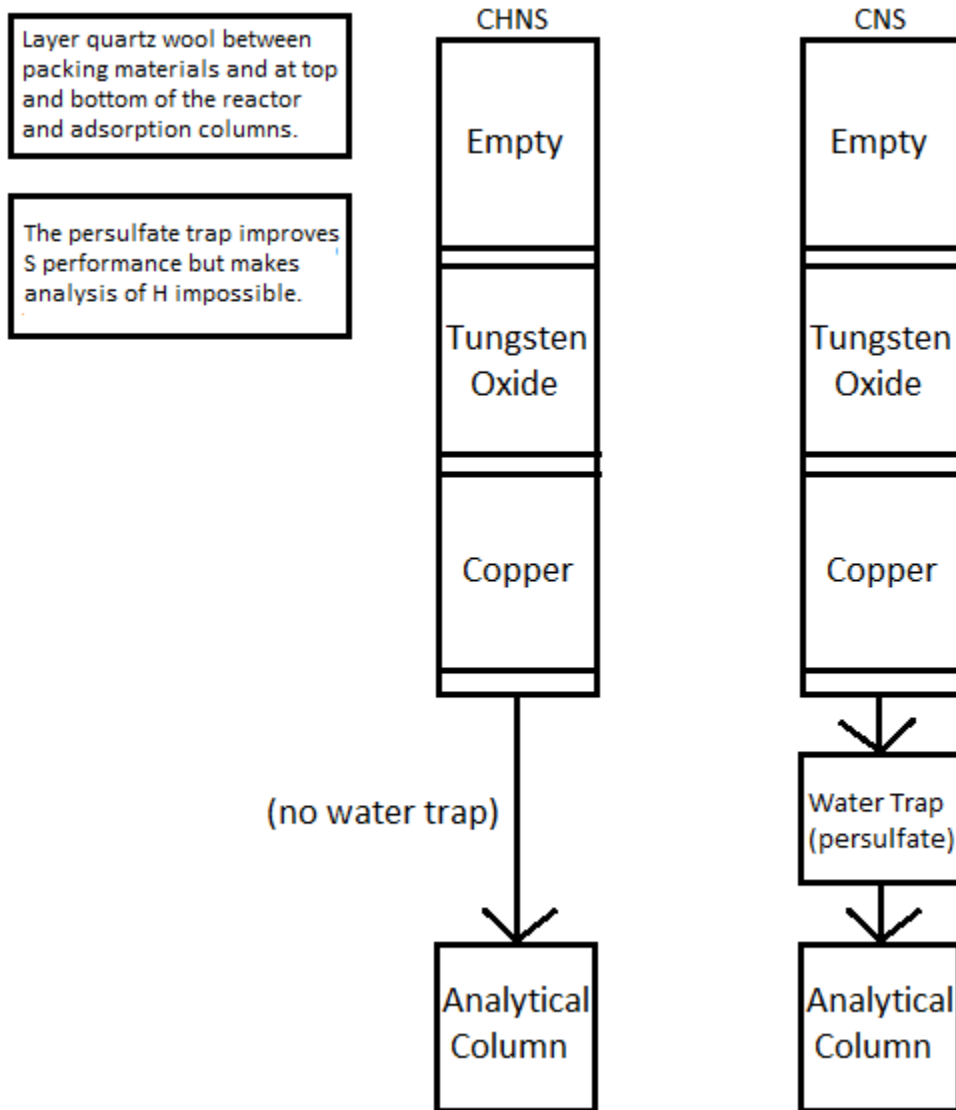


Figure 3: Analytical equipment setup based on desired elements.

Properties of reactor materials and adsorption filter: Copper oxide/chromium oxide: Creates an oxidizing environment during combustion of the sample. Vanadium pentoxide: Catalyzes the combustion of S (as sediment ion sulfate/sulfides) to sulfur dioxide. Tungsten oxide (WO_3): Helps complete the oxidation of combustion products to final products.

Electrolytic copper: Reduces potentially formed nitrogen oxides and sulfur trioxide combustion products to elemental nitrogen and sulfur dioxide. Silvered cobaltous/cobaltic oxide: Catalyst used to remove sulfur dioxide and halogens. Magnesium perchlorate (anhydrous): Desiccant which removes water (i.e., combusted H) in the adsorption filter.

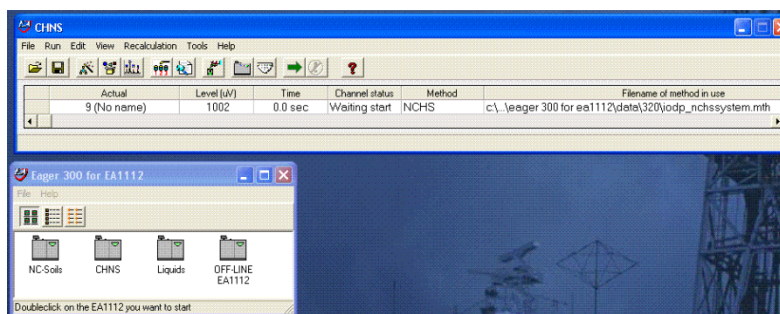


Figure 4. Eager 3000 CHNS Screen.

Verifying Instrument Calibration

The CHNS instrument is calibrated at the beginning of each expedition (see *Quality Assurance/Quality Control*). Calibration is verified before running each sample sequence by running a blank and a calibration verification standard against the current calibration curve.

Reset the Calibration Factor

1. On the *CHNS* screen, select **Recalculation > Reset Calculation Factors** and then click **OK**.
2. Double-click on **CHNS.exe** and enter LIMS user name and password to activate *CHNS Loader*.
3. Select the **Output Sample from LIMS** tab.
4. Select calibration standards, which have analysis codes **CHNS QAQC** and verification code **Standard**, with one blank to be run in the next batch or sequence.
5. Row number (located at the right bottom of the window) must be **1**.
6. Click **Export** to create the LIMS file.
7. Save LIMS file into the folder where you saved the method.

Upload LIMS file to Eager 300 software

1. On the *CHNS* screen, select **Edit > Sample table**.
2. From the menu at the top of the sample table, select **Edit sample > Import sample table from LIMS**.
3. Select an appropriate file and click **OK** to upload file.
4. Click **Cancel** to escape the window.

Edit the calibration curve sample table (Figure 4)

1. Select an appropriate standard name (e.g., **Sulfanilamide**).
2. Ensure the order of the container number (see the end of *Filename*) is correct.
3. Click **OK** to close window.
4. Select **File > Save Method** on the *CHNS* screen to save changes. (Calibration data will be saved into LIMS with the first batch of unknown sample measurements.)
5. On the *CHNS* screen, click the green arrow toolbar icon to analyze the blank and standards.
6. Confirm blank: during the blank run, select **View > View sample being acquired** from the *CHNS* screen. If the chromatogram has unexpected peaks or a disturbed baseline, the cause of this problem must be determined before unknown samples can be run.

Confirm the Calibration Curve (Figure 5)

1. On the *CHNS* screen select **View > View Calibration curve**.
2. Click **Component** to change curve components (color of selected component will change to blue).
3. Check calibration factor.

Calibration method can be changed on this screen. For more information see the FlashEA 1112 Operating Manual (p. 232). If the calibration factor is acceptable (see [Quality Assurance/Quality Control](#)), unknown samples can be run. If the calibration factor is outside of control limits, the laboratory technician will edit the component table and integration parameters and recalculate the calibration factor.

	A	Sample name	Filename	Type	Standard name	Weight	Protein F	Category	Sampler method filename
1	Act.	BLANK	BLANK	Bypass					
2		OTHR468933	OTHR468933-2	Std	Sulfanilamide	4.62			
3		OTHR163945	OTHR463945-3	Std	Sulfanilamide	4.36			
4		OTHR432581	OTHR432581-4	Std	Sulfanilamide	6.88			
5		OTHR397542	OTHR397542-5	Std	Sulfanilamide	6.98			
6		OTHR468792	OTHR468792-6	Std	Sulfanilamide	10.31			
7		OTHR761358	OTHR761358-7	Std	Sulfanilamide	9.98			
8									
9									
10									
11									

Figure 5. Sample Table.

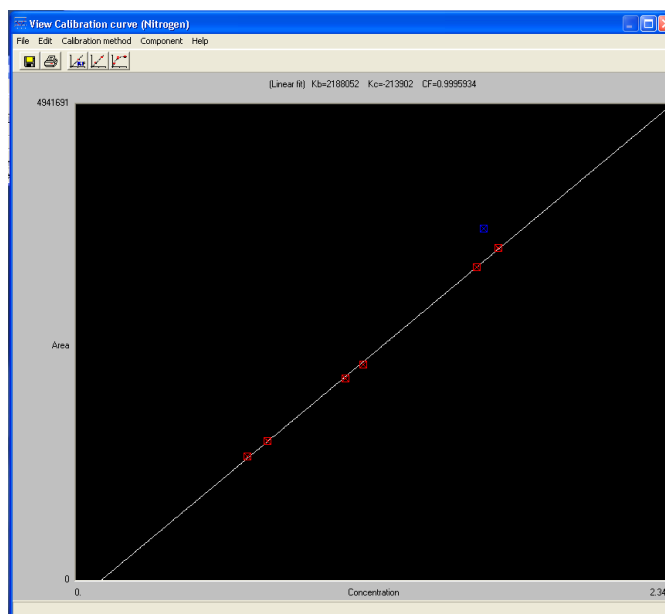


Figure 6. Calibration Curve.

Creating the Sample Table

1. Double-click on **CHNS.exe**.
2. Enter the LIMS user name and password to activate *CHNS Loader*.
3. Open the **Output Sample from LIMS** tab.
4. Click column header **Container** (samples are sorted by container number).
5. Select samples to be run in the next batch or sequence.
6. Adjust row index. Row index number must be the same as the row number that is two rows below the last sample in the current sequence table of the *Eager 300* software.
7. Click **Export** and save file to the folder where you saved the method.
8. Exit the *CHNS Loader*.

Uploading the Sample Table to *Eager 300* Software

1. On the *CHMS* screen, select **Edit > Sample table**.
2. From the menu at the top of the sample table, select **Edit sample > Import sample table from LIMS** (Figure 6Figure 7).
3. Select appropriate LIMS file, and click **OK** to upload file.
4. Click **Cancel** to escape the window.
5. Make sure sample holder number is correct.

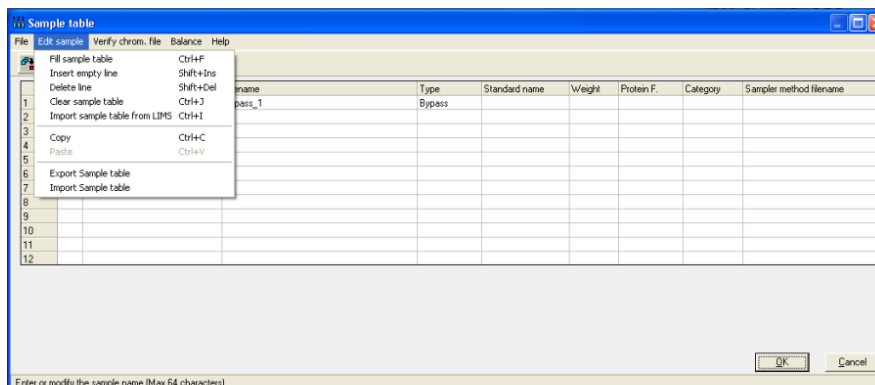


Figure 7. Edit Sample Menu.

Running Samples

1. To start running samples, click the green arrow toolbar icon on the *CHMS* screen.
2. To monitor the acquisition status, select **View > View sample being acquired** (Figure 7Figure 8).
3. Once samples are run, **View Chromatograms** shows a single selected chromatogram; **Overlay Chromatograms** is better suited for comparison of chromatograms (maximum of five).

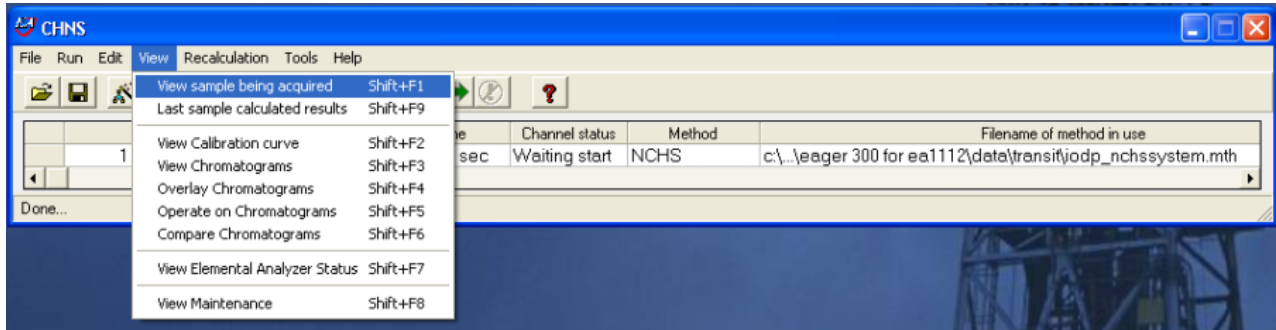


Figure 8. View Menu.

Analyzing Data

QA/QC data is captured by LIMS, but the technician should monitor QC values from the calibration verification (CV) standards and determine if corrective action should be taken.

After analyzing the standard and checking the instrument precision, complete the following steps.

1. On the *CHNS* screen, select **Recalculation > Summarize results** (*Figure 8Figure 9*).
2. Select a group of samples to calculate the standard deviation for by indicating a group number (1) in the Group column of the *Summarize results* table. For example, in *Figure 8 Figure 9* the 6 sulfanilamide standards are grouped (1) for standard deviation analysis.
3. With the mouse, select the first row of a group (Row 2 in *Figure 8Figure 9*) and select **View > Statistical Calculation** to see statistical data calculated for that group.

Summarize results (Element %)

File Edit View Print Help

Nitrogen%

	Group	Sample name	Filename	Inj Date	Inj Time	Type	Weight	Protein Factor	None	AS	Vial	Nitrogen%	Carbon%	Hydrogen%	Sulphur%
1	0	Bypass	Bypass	02/14/2009	16:56	By-Pass						0	0	0	0
2	1	ST_OTHR46	ST_OTHR46	02/14/2009	22:27	Blank						0	0	0	0
3	1	ST_OTHR46	ST_OTHR46	02/14/2009	22:37	STD	4.9316	1	1			16.2700005	41.8400002	0	18.6200008
4	1	ST_OTHR46	ST_OTHR46	02/14/2009	22:47	STD	6.295	1	1			16.2700005	41.8400002	0	18.6200008
5	1	ST_OTHR46	ST_OTHR46	02/14/2009	22:57	STD	7.1297	1	1			16.2700005	41.8400002	0	18.6200008
6	1	ST_OTHR46	ST_OTHR46	02/14/2009	23:07	STD	9.9814	1	1			16.2700005	41.8400002	0	18.6200008
7	1	ST_OTHR46	ST_OTHR46	02/14/2009	23:17	STD	10.7989	1	1			16.2700005	41.8400002	0	18.6200008
8	1	ST_OTHR46	ST_OTHR46	02/14/2009	23:27	STD	4.0533	1	1			16.2700005	41.8400002	0	18.6200008
9															
10															
11															
12															
13															

Enter or modify the sample group (It's used to group samples for calculation of average or std etc.)

Figure 9. Summarize Results Screen.

Quality Assurance/Quality Control

A program of quality assurance/quality control (QA/QC) ensures that a measurement system is performing within control limits and therefore provides high-quality data. The QA/QC program for this system includes instrument calibration and calibration verification, blank verification, and accuracy and precision monitoring.

Instrument Calibration

The CHNS instrument is calibrated by the chemistry technician at the beginning of the expedition. Calibration is verified routinely during operation by running calibration verification standards (see *Calibration Verification*).

Sequence

An analytical sequence is a group of sample runs sharing a calibration curve, blanks, reference materials, and verification samples. One sequence (table) allows a maximum of 200 samples.

Analytical Batch

An analytical batch is a group of samples run together. Each CHNS batch of unknown samples contains a calibration verification sample, calibration blank, and known sample.

Calibration Blank

A calibration blank run each sequence consists of a tin cup containing only reagent V_2O_5 catalyst to assess the effect that the tin cup and catalyst have on the analysis results. If the blank chromatogram has unexpected peaks or a disturbed baseline, the cause of this problem must be determined before unknown samples can be run. Notify the chemistry technician.

Calibration Verification

The calibration verification standard, also called the QC check standard, is run with each analytical batch and contains 0.6–0.7 g of BBOT in a tin cup with V_2O_5 catalyst. If the calibration factor is within control limits, unknown samples can be run. If the calibration factor is outside of control limits, edit the component table and integration parameters and recalculate the calibration factor. Poor calibration verification results can also indicate degradation of the reactor. If calibration cannot be verified, notify the onboard laboratory specialist.

Precision

Precision is the degree to which further measurements will show the same or similar results. To analyze for precision on this system, a standard (sulfanilamide, BBOT, or aspartic acid) is run in duplicate or triplicate and the standard deviation of the results calculated for each element:

$$s = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N-1}}$$

where \bar{x} = average of results, and N = number of data points.

Accuracy

Accuracy is the degree of closeness of a measured value to the actual (true) value. A standard of sulfanilamide in a tin cup with V_2O_5 catalyst is run with each sequence to verify accuracy. Results of the standard must be within $\pm 10\%$ of true values for the system to be considered in control. Sulfanilamide true values and control limits:

- C = 41.848% (37.663%–46.033%)
- H = 4.685% (4.217%–5.154%)
- N = 16.267% (14.640%–17.894%)
- S = 18.620% (16.758%–20.482%)
- O = 18.582% (16.724%–20.440%)
- Other materials (e.g., USGS reference sediments) can be used to measure accuracy, so long as their values are known.

LIMS Integration

Sample/Analysis Components

Analysis code	Component name	Unit	Definition
CHNS	carbon_percent	wt%	Carbon concentration in sample
	container_number	—	Number assigned to weighed sample
	dat_asman_id	—	ASMAN serial number for data file
	dat_filename	—	Filename of data file
	hydrogen_percent	wt%	Hydrogen concentration in sample
	mass	mg	Mass of sample
	nitrogen_percent	wt%	Nitrogen concentration in sample
	run_test	—	Test number of related calibration
	sulfur_percent	wt%	Sulfur concentration in sample

When uploading data enter the term "Rejected" in place of the value for an elemental concentration for a sample or series of samples that followed a running standard in which the analytical error exceeded the QA/QC limits (10% for each element). This displays "Rejected" in LIMS/LORE for only that specific sample element and still keeps intact the excel file containing the raw data which is uploaded to the database.

Health, Safety, & Environment

Safety

General

- Before using the gases, chemicals, and filling materials required for this procedure, carefully read the MSDS for that material.
- Proper personal protective equipment must be used for handling all apparatus and materials in this procedure.
- The instrument has a safety cutoff feature that cuts power to the furnace heating elements if the instrument malfunctions due to a component failure or abnormal operating conditions. If the red safety LED indicator on the synoptic panel is illuminated, contact laboratory staff immediately.

Warnings

- **WARNING!** Do not open the furnace compartment during operation.
- **WARNING:** Do not touch either furnace when the furnace temperature is higher than 40°C. Furnace temperature is shown in the *EA 1112 Status* screen (Select **View > View Elemental Analyzer Status**).
- **WARNING:** Do not open the protection panel. The gas chromatographic column may only be serviced by the shipboard technicians.

Compressed Gases

- Gas cylinders are pressure hazards and should be changed only by shipboard staff. High-pressure gas lines can be hazardous if there are leaks, particularly the oxygen line.
- United States standards for inert gas and oxidation regulators exist to physically prevent the user from hooking an oxidizing gas (e.g., O₂) to an inert gas line and vice versa. Always use the appropriate CGA fitting for each gas! The JRSO uses the following fitting types for the gases used in this method:
 - Inert Gas (Helium): CGA 580 (male, right-hand threading)
 - Oxidizing Gas (Oxygen): CGA 540 (female, right-hand threading)
- Adapters do exist to convert one gas fitting to another: do not use them! The gender and threading direction of the standard fittings are designed to protect the user.
- Gas cylinders should always be restrained at two points by a strap or chain. In the case of single cylinders at use in the laboratory, do not share a strap or chain between two cylinders: each cylinder should have its own restraining gear. In the case of the gas racks in the hold, consult with the Laboratory Officer before attempting to separate a gas cylinder from the rack.
- Specific Gas Descriptions
- Oxygen is an odorless colorless gas that is a strong oxidizer. An oxygen leak could cause spontaneous combustion if an organic source is at hand. Always check the O₂ lines for leaks. Appropriate precautions should be taken.
- Helium is an odorless colorless inert gas. Rapid release of He from a cylinder could potentially asphyxiate the user, so appropriate precautions should be taken.

Chemical Safety

Many of the chemicals used in the CHNS procedure, including the standards, present potential chemical hazards. Always read the material safety data sheet (MSDS) of each and every chemical before working with them. Some of the highest-hazard chemicals are summarized below:

Magnesium Perchlorate

Extremely Strong Oxidizer!; keep away from organic materials and mineral acids
Air and Water Reactive!

- Highly exothermic upon addition of water
- Absorbs water from air
- May explode under prolonged exposure to heat
- Will increase intensity of a fire

Health hazard:

- Inhalation: irritant
- Contact: irritant
- Ingestion: abdominal pain, vomiting, diarrhea, may be fatal

Vanadium Pentoxide

Extremely toxic! Always use the appropriate personal protective equipment (PPE) and environmental controls when using this chemical.

- **Harmful if swallowed or inhaled**
- **Causes serious eye damage**
- **May cause respiratory irritation**
- **Suspected of causing genetic defects, damaging fertility, and/or harm of the unborn child**

- **Causes damage to internal organs through prolonged or repeated exposure**
- **Toxic to aquatic life with long-lasting effects**

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Pollution Prevention

Degree of pollution according to IEC 664 = 2

Waste Management

This procedure generates no waste for disposal beyond the standard chemistry laboratory protocols..