

ELEMENTAL ANALYZER (CHNS)

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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.

Keywords: Carbon, Nitrogen, Hydrogen, Sulfur

Carbon Analysis Nitrogen 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 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 organ-ic 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 com-mon 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 meta-bolic 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 (H₂S = H₂S(aq) + 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 ev-

idence 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 SO₄ reduction. Elemental sulfur enrichments may form at places where the sulfide concentrations were high, resulting from in situ SO₄^{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 (Stot/Corg 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 Corg 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, postdepositional sulfidization of Corg-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 V₂O₅ 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 N₂, CO₂, H₂O, and SO₂ 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.