Determination of Total Organic Carbon in Sediment
(Lloyd Kahn Method)
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1. Scope and Application

    1.1   This method describes protocols for the determination of organic carbon in ocean sediments.

    1.2   Although the detection limit ma vary with procedure or instrument, a minimum reporting value of 100 mg/kg will be required for the ocean dumping/dredging program.

    1.3   Several types of determinations, which are considered equivalent are presented.

    1.4   Data are reported in mg/kg on a dry weight basis.

    1.5   Wet combustion methods are not considered to be equivalent to the pyrolytic methods herein described.

2. Summary of Method

    2.1   Inorganic carbon from carbonates and bicarbonates is removed by acid treatment.

    2.2   The organic compounds are decomposed by pyrolysis in the presence of oxygen or air.

    2.3   The carbon dioxide that is formed is determined by direct nondispersive infrared detection, flame ionization gas chromatography after catalytic conversion of the carbon dioxide to methane; thermal conductivity gas chromatography, differential thermal conductivity detection by sequential removal of water and carbon dioxide; or thermal conductivity detection following removal of water with magnesium perchlorate.

3. Sample Handling and Preservation

    3.1   Collect sediments in glass jars with Teflon or aluminum foil. Cool and maintain at 4ºC. Analyze within 14 days.

4. Interferences

    4.1   Volatile organics in the sediments may be lost in the decarbonation step resulting in a low bias.

    4.2   Bacterial decomposition and volatilization of the organic compounds are minimized by maintaining the sample at 4ºC, analyzing within the specified holding time, and analyzing the wet sample.

5. Apparatus

   5.1   Drying oven maintained at 103º-105ºC.

   5.2   Analytical instrument options:

   5.2.1   Perkin Elmer Model 240C Elemental Analyzer or equivalent.

   5.2.1.1 In this instrument, the sample from Section 7.2 is pyrolyzed under pure oxygen, water is removed by magnesium perchlorate and the carbon dioxide is removed by ascarite. The decrease in signal obtained by differential thermal conductivity detectors placed between the combustion gas stream before and after the ascarite tube is a measure of the organic carbon content.

   5.2.2   Carlo Erba Model 1106-CHN Analyzer or equivalent.

   5.2.2.1 In this apparatus, the sample is pyrolyzed in an induction type furnace, and the resultant carbon dioxide is chromatographically separated and analyzed by a differential thermal conductivity detector.

   5.2.3   LECO Models WR-12, WR-112, or CR-12 carbon determinators or Models 600 or 800 CHN analyzers.

   5.2.3.1 In the LECO WR-12, the sample is burned in a high frequency induction furnace, the carbon dioxide is selectively adsorbed at room temperature in a molecular sieve. It is subsequently released by heating and is measured by a thermal conductivity detector. The WR-112 is an upgraded WR-12 employing microprocessor electronics and a printer to replace the electronic digital voltmeter.

   5.2.3.2 In the LECO CR-12 carbon determinator, the sample is combusted in oxygen, moisture and dust are removed by appropriate traps and the carbon dioxide is measured by a selective, solid state, infrared microprocessor and the carbon content is displayed on a digital readout and recorded on an integral printer.

   5.2.3.3 In the LECO CHN-600 and CHN-800 elemental analyzers, the sample is burned under oxygen in a resistance furnace and the carbon dioxide is measured by a selective infrared detector.

   5.2.4   Dohrman Model DC-85 Digital High Temperature TOC Analyzer

   5.2.4.1 In this instrument, the sample is burned in a resistance furnace under oxygen, the interfering gases are removed by a sparger/scrubber system and the carbon dioxide is measured by non-dispersive infrared detectors and shown on a digital display in concentration units.

5.3 No specific analyzer is recommended as superior. The above listing is for information only and is not intended to restrict the use of other unlisted instruments capable of analyzing TOC. The instruments to be used must have the following specifications:

5.3.1 A combustion boat which is heated in a stream of oxygen or air in a resistance or induction-type furnace to completely convert organic substances to CO_2 and water.

5.3.2 A means to physically or by measurement technique to separate water and other interferants from CO_2.

5.3.3 A means to quantitatively determine CO2 with adequate sensitivity (100 mg/kg), and precision (25% at the 95% confidence level as demonstrated by repetitive measurements of a well mixed ocean sediment sample).

5.4 A strip chart or other permanent recording device to document the analysis.

6. Reagents

6.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the carbon concentration of the blank.

6.2 Potassium hydrogen phthalate, stock solution, 100 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary standard Grade) in distilled water and dilute to 100.0 ml.

6.3 Potassium hydrogen phthalate, standard solutions: prepare standard solutions from the stock solution by dilutions with distilled water.

6.4 Phosphoric acid solution, 1:1 by volume.

7. Procedure

7.1 Weigh the well mixed sample (up to 500 mg) into the combustion boat or cup. Add 1:1 phosphoric acid drop-wise until effervescence stops. Heat to 75ºC.

7.2 Analyze the residue according to the instrument manufacturer's instructions.

7.3 Determine percent residue on a separate sample aliquot as follows:

7.3.1 Heat a clean 25 ml beaker at 103-105ºC for one hour. Cool in desiccator, weigh to the nearest mg and store in desiccator until use.

7.3.2 Add 1 g, weighed to the nearest mg, of an aliquot of the well-mixed sample.

7.3.3   Dry and heat in the 103-105ºC oven for 1 hour. Cool in desiccator. Weigh to the nearest mg.

8. Calibration

8.1   Follow instrument manufacturer's instructions.

8.2   Prepare calibration curve plotting mg carbon vs. instrument response, using 4 standards and a blank covering the analytical range of interest.

9. Precision and Accuracy:

9.1   The precision and accuracy will differ with the various instruments and matrices and must be determined by the laboratories reporting the data. To initiate a control chart, a representative sample of well-mixed sediment should be analyzed 15 times to determine the analytical precision. Set up a control chart showing 3 times the standard deviation limits for precision.

9.2   Subsequently during analysis of environmental samples, take one sample per batch of 20 or less and run in quadruplicate. Calculate standard deviation and report with initial control chart data.

9.3   If the sample being run in quadruplicate exceeds the 3 standard deviation limit, identify error and rerun environmental samples in that batch alone with the quadruplicate sample.