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## NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 1998.08

September 29, 1998

To: E

From: Robert S. Williams, Jr., Chief  
National Water Quality Laboratory

Subject: Change in the Analytical Method Used for the Determination of Inorganic Carbon in Sediment

Effective date  
of changes: September 29, 1998

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Revision: None

### SCOPE

The National Water Quality Laboratory (NWQL) has historically determined inorganic carbon in sediment by method O-5102-83 as described by Wershaw and others (1987). There are two lab codes, and two WATSTORE and method codes for this method. Lab code 503, WATSTORE code 00686, and method Code C are for unsieved samples. Lab code 5051, WATSTORE code 49270, and method code D are for sieved samples.

This method is a classic gasometric technique, but improved techniques are currently (1998) available. The USGS Geologic Division (GD) uses a coulometric method for the determination of inorganic carbon (carbonate carbon) in geologic materials. Brandt and others (1990) described this method. The NWQL will implement this method to determine inorganic carbon in sediment beginning October 1, 1998.

The new lab code for unsieved samples will be 2321, and the new method code will be E. The new lab code for sieved samples will be 2319, and the new method code will be E. The WATSTORE codes will remain unchanged. The preliminary method detection limit (MDL), which was determined by the procedure described by the U.S. Environmental Protection Agency (1992), is 0.1 g/kg and the method report limit is 0.2 g/kg.

Organic carbon in sediment is calculated as the difference between total carbon and inorganic carbon. The lab code and method code for organic carbon must also change because the method for inorganic carbon is changing. The new lab code for sieved sample organic carbon in sediment is 2320, and the new method code is C. Organic carbon in unsieved samples is not reported by NWQL because the subtraction is performed by the customer. The method for total carbon in sediment will not be changed.

An expanded version of this tech memo, including all the data used in this work, will be made available on the NWQL Home Page as a technical paper at <http://www.nwql.cr.usgs.gov/USGS>. This paper should be available by January 1, 1999.

## **Background**

The NWQL has used the traditional gasometric technique since the 1970's. This method is labor intensive and lacks the reproducibility of more modern techniques. The GD has a technique that uses perchloric acid to release carbon dioxide, which is coulometrically titrated using platinum and silver/potassium iodide electrodes (Jackson and others, 1987). The NWQL will implement this method except hydrochloric acid will be used to release the carbon dioxide. Hydrochloric acid was chosen over perchloric acid for the following reasons:

- 1) Perchloric acid is a stronger oxidizer than hydrochloric acid, and there was concern that perchloric might oxidize some of the organic carbon in bed sediment, leading to a high bias; and
- 2) Hydrochloric acid is much safer to use in the laboratory.

Before the NWQL could implement this method, the following requirements had to be demonstrated:

- 1) The coulometric technique with hydrochloric acid (coulometric/hydrochloric acid) must produce equivalent results to the coulometric technique with perchloric acid (coulometric/perchloric acid), when both methods are used for analysis of bed-sediment samples.
- 2) The coulometric/hydrochloric acid technique must accurately analyze Standard Reference Materials (SRM) and Geologic Division Reference Materials (GDRM).
- 3) Results produced by the coulometric/hydrochloric acid and the gasometric methods must be described and compared.
- 4) A preliminary MDL must be determined, and a method reporting limit (nondetected value) must be produced. Duplicate precision for the coulometric/hydrochloric acid method must be provided.

## **Discussion of Results**

The NWQL and the GD analyze different size fractions of bed-sediment samples collected by the National Water-Quality Assessment Program (NAWQA). The GD analyzes samples sieved at <63 micrometers and the NWQL analyzes samples sieved at 2 millimeters.

Eight GD NAWQA bed-sediment samples were analyzed by the coulometric/hydrochloric acid technique and the coulometric/perchloric acid techniques. A two-tailed paired T-test demonstrated that there was no significant difference in the means of the two data sets at the 0.05 significance level. The results of the F-test demonstrated that there was no significant difference in the variances at the 0.05 significance level.

Results from the analysis of reference materials by the coulometric/hydrochloric acid technique are presented as follows:

[SRM, Standard Reference Material; GDRM, Geologic Division Reference Material; g/kg, gram per kilogram; %, percent]

Name	Type	Source	Reference value, g/kg	Mean analyzed value, g/kg	Number analyses	Relative standard deviation, %	Ratio of analyzed value to reference value, %
GSD-1	SRM	China bed sediment	14.8	15.1	7	4.7	102.7
GSS-8	SRM	China soil	16.3	15.1	7	9.5	103.2
BCSS-1	GDRM	Canada marine sediment	0.6	0.7	7	5.7	85.7
MAG-1	GDRM	Maine marine mud	1.2	1.1	7	6.4	88.6
SDO-1	GDRM	Kentucky shale	2.8	1.3	9	10.0	59.6

The results for soil, bed sediments, and marine mud demonstrated that the analyzed concentrations were within 85 to 103 percent of the reference concentration. The absolute difference between the mean analyzed concentration and the reference concentration was never greater than 0.5 g/kg. The relative standard deviation (RSD) ranged from 4.7 to 9.5 percent. However, the analysis of a Kentucky shale sample only recovered about 60 percent of the reference concentration and had an RSD of 10 percent.

Thirty bed-sediment samples that had been analyzed by the gasometric method were reanalyzed by the coulometric/hydrochloric acid method to compare results and project impacts on the database. The regression analysis formula was:

$$Y = 1.13X + 1.13$$

where Y = coulometric results and  
X = gasometric results

The correlation coefficient was 0.997, indicating a strong correlation between the results of the two methods. However, the slope of the regression equation demonstrated that the results from the coulometric method were about 13 percent higher than the results from the gasometric method. A

two-tailed paired T-test demonstrated that this bias was significant at the 0.05 significance level. An F-test demonstrated that the variation in the two methods was insignificant at the 0.05 significance level.

In addition, two GDRMs were analyzed to determine which method produced the most accurate results. The coulometric/hydrochloric acid method recovered from 80 to 89 percent of the referenced concentrations, while the gasometric technique recovered only 50 to 77 percent of the referenced concentrations.

Seven NAWQA sediments were analyzed in duplicate to describe precision for the coulometric/hydrochloric acid technique. The average agreement between duplicates was 97.1 +/- 3.9 percent. The average difference between duplicates was -0.1 g/kg, the absolute value of which is less than the method reporting limit of 0.2 g/kg.

Seven replicates of the Canada marine sediment (BCSS-1) were analyzed to calculate an MDL. The preliminary MDL was calculated to be 0.1 g/kg, and the method reporting limit (nondetected value) is 0.2 g/kg.

## **Conclusions**

The coulometric/hydrochloric acid method will produce results equivalent to the coulometric/perchloric acid technique when analyzing soils, bed sediments, and marine mud. However, perchloric acid must be used when analyzing shales because hydrochloric acid will not produce accurate results. Shales apparently need a more vigorous digestion with a stronger acid to obtain accurate results. The NWQL analysis is designed for stream, lake and ocean sediment samples only and not for the analysis of samples that are predominantly shale or other rock materials. The duplicate precision of the coulometric/hydrochloric acid method is acceptable.

The coulometric/hydrochloric acid method demonstrated a 13 percent high bias when compared to the gasometric method. Analysis of GDRM demonstrated that the coulometric/hydrochloric acid technique consistently delivered more accurate results than the gasometric technique. The intercept of the regression equation predicts that the coulometric/hydrochloric acid method has a blank that is about 1.1 g/kg higher than the blank from the gasometric method. However, the analysis of low-level samples did not demonstrate this difference. Therefore, the difference is probably an anomaly produced by the least squares method of regression analysis.

## **Impact on data base**

There will be an average 13 percent increase in the historical inorganic carbon concentrations as soon as this method is implemented. No change in the variance is expected. Organic carbon in sediment is calculated as the difference between total carbon and inorganic carbon in sediment. When the new method is implemented, an increase in inorganic carbon concentrations will result in a corresponding decrease in organic carbon concentrations.

## **Selected References**

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Jackson, L.L., Brown F.W., and Neil, S.T., 1987, Major and minor elements requiring individual determination, classical whole rock analysis and rapid rock analysis, in Baedeker, P.A., ed., Methods for geochemical analysis: U.S. Geological Survey Bulletin 1770.

U.S. Environmental Protection Agency, 1992, Primary drinking-water regulations, maximum contaminant levels (appendix B of part 136, Definition and procedure for the determination of the method detection limit-Revision 1.11): U.S. Code of Federal Regulations, Title 40, parts 100-149, revised as of July 1, 1992, p. 565-567.

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Supersedes: None

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Distribution E and <http://wwwnwql.cr.usgs.gov/USGS>