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DEVELOPMENT OF A COLOURED WATER CRM FOR SULFATE ANALYSIS

by

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ABSTRACT

This report describes the development of the first coloured water Certified Reference Material (CRM) for sulfate analysis. The material is a mixture of filtered waters from several different locations known to be contaminated with coloured organic matter. Homogenization and subsampling procedures were described for the CRM, which has a volume of 1000 litres and is stored at 4°C. Analytical data from several sources were found compatible and were combined for deriving a reference value of 2.77 ± 0.16 mg SO_4/L. This reference water has been shown to be stable for 18 months and its long-term stability will be continuously monitored.

EXECUTIVE SUMMARY

Due to coloured interferents in the analysis of coloured waters, some methodologies have produced biased sulfate results, which have subsequently lead to biased conclusions. A pertinent reference material would help alleviate this situation as it provides a reference value, to which the intra- or inter- laboratory quality control can be compared. This report describes the development of such a coloured water certified reference material for SO_4 analysis. The recommended value is 2.77±0.16 mg SO_4/L.

INTRODUCTION

Sulfate data generated from coloured waters by the various methodologies[1-2] are not always compatible due to interferences from the coloured matter in the waters. This is well evidenced by a recent interlaboratory study[3], where some methodologies were assessed as producing biased results. The data incompatibility and the fact that SO_4 data are important in the study of acid rain have created a great deal of discussion and concern over the analysis of SO_4 in coloured waters.

A coloured water Certified Reference Material (CRM) would be a useful quality control sample in routine analysis, or a reference sample in intercalibration exercise and method validation. To our knowledge, there is no such CRM anywhere. This report describes the preparation and development of the first coloured water CRM.

PREPARATION OF THE CRM

Containers

Several 100 L polyethylene containers, purchased from CANBAR Products Ltd., were cleaned and used to collect many different waters. The CRM tank, with a capacity of about 1200 L, was also purchased from CANBAR and cleaned according to the cleaning procedure for major ion containers[4]. In brief, it was cleaned with hot tap water and chromerge, followed by rinsing five times each with hot tap water and deionized distilled water. The tank was then filled with deionized distilled water and allowed to stand for several weeks before use.

Sample Treatment

Several natural coloured waters were collected from different locations in the Atlantic and Ontario regions. Each water was filtered through 0.45 µm filter paper and all the filtrate was transferred into a clean CRM tank in the 4°C room. The filtered water was homogenized with a simple closed circuit mixing system, consisting of a pump (Fasco Industry Inc., Model F78), a glass tube (I.D. ~1 cm, barrel height long) and an inert pliable rubber tube. The glass tube was attached to the entry end of the pump, whereas the rubber tube connected to the exit end of the pump. The glass tube was then inserted into the barrel to 3/4 of the water depth. The pump was then primed from the exit end using a priming bulb. After priming, the bulb was removed and the rubber end inserted into the barrel to 1/4 of the water depth. The pump was allowed to run for eight hours to provide continuous mixing.

At the end of the homogenization period, an initial subsampling was made directly into six test bottles via the rubber tube: two bottles for subsampling from the top section of the barrel, two from the middle, and two from the bottom part. The six subsamples were used for testing the homogeneity of the CRM. The homogenized and filtered reference water in the CRM tank is identified as CRM-94 and stored at 4°C in the dark.

RESULTS AND CONCLUSION

Physical and Chemical Properties

Table 1 summarizes the main physical and chemical properties of the CRM. The properties are in the useful concentration range for interlaboratory QC studies for the Long Range Transport of Atmospheric Pollutants (LRTAP) Program.

Homogeneity Test

The six subsamples described above were analyzed for SO_4 and the results were treated by the two-way analysis of variance to establish homogeneity. This procedure was previously used for testing the homogeneity of a sediment CRM[5]. Table 2 presents current results, which indicate bulk sample homogeneity as the experimental F values are much smaller than the corresponding critical F values.

Colorimetric Data

The colorimetric data were generated by the Methyl Thymol Blue (MTB) colorimetry method[6]. Due to interferences from the coloured matter in the water, the colorimetric results were expected to be biased high[1-2]. Indeed, the average result from the untreated water (6.6 ppm) was two times greater than that from the pretreated water (3.3 ppm). The pretreatment of the water was made by the H_2O_2/UV oxidation procedure[6], which destroyed the coloured matter thus rendering the water colourless and minimizing the interferences. The pretreatment also oxidized the reduced forms of sulfur to produce more SO_4 in addition to the original dissolved SO_4; the total of these sulfates was measured to be 3.3 ppm. Thus, the bias due to interferences is at least 100% higher than the true SO_4 value. Consequently, the colorimetric data cannot be used in the derivation of SO_4 reference value.

Ion Chromatographic Data and Stability

The IC data were generated using an in-house automated system connected to a Dionex 2110 ion chromatograph. Some two hundred direct analyses were made. In addition to these, more data were also generated from the multiple standard addition technique, which gave excellent recoveries: 99.5% at the first addition, 100% at the second addition, and 100.1% at the third addition. These two types of data (direct analysis and standard additions) were found to be compatible, which confirms reliability of IC data[6].

The SO_4 content has been monitored periodically for 18 months and has indicated that the CRM is stable.

Reference Value

Additional IC data were generated from three different interlaboratory studies[3,7,8]. Furthermore, the data generated by a commercial laboratory using turbidimetry technique agreed with the interlaboratory and in-house data. The combined data totalled to more than 300 observations, yielding a reference value of 2.77±0.16 mg SO_4/L.

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TABLE 1 Physical and Chemical Properties of the CRM

Constituent	Value
Colour, H.U.	140
Specific conductance, μMHO/cm	36
pH	6
Total alkalinity, mg $CaCO_3$/L	3.4
Sodium, mg/L	4
Potassium, mg/L	0.3
Calcium, mg/L	1.8
Magnesium, mg/L	0.7
Sulfate, mg/L	2.7
Chloride, mg/L	5
Dissolved Organic Carbon, mg C/L	12

TABLE 2 Results of Analysis of Variance of SO_4 Data (mg/L)

Replicate	Samples*					
	B-1	B-2	M-1	M-2	T-1	T-2
1	2.858	2.782	2.789	2.815	2.664	2.635
2	2.740	2.806	2.655	2.639	2.763	2.722
3	2.730	2.617	2.787	2.647	2.843	2.665
4	2.708	2.789	2.692	2.745	2.693	2.657
5	2.702	2.838	2.720	2.776	2.741	2.728

Overall mean = 2.732
Overall variance = 0.0044
F_{column} = 0.826 versus $F_{critical}$ = 2.71
F_{row} = 0.519 versus $F_{critical}$ = 2.78

*B, M and T refer to Bottom, Middle and Top samples, respectively.

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