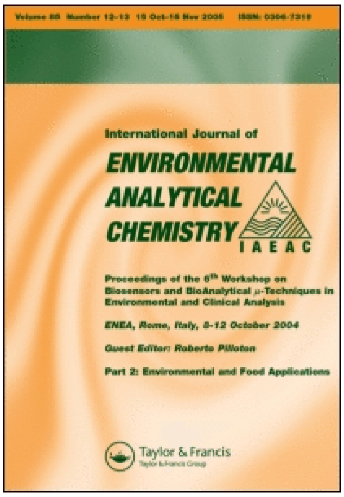

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A Comparison of the Gravimetric and X-Ray Fluorescence Methods for the Determination of Sulfur in Aqueous Mixtures Resembling Seawater[†]

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KEY WORDS: X-ray, sulfur, seawater.

The use of X-ray fluorescence spectrometry is described as a means of determination of total sulfur concentration of aqueous mixtures. The results of X-ray analyses of several types of solutions are compared to the results obtained by the gravimetric methods of barium sulfate precipitation. Sample pretreatment and handling were minimized by the X-ray method. Solutions containing sodium and chloride ion concentrations resembling those found in natural seawater were found to be especially amenable to total sulfur determination by X-ray fluorescence analysis.

INTRODUCTION

The evolution of scientific apparatus in recent years has led to improvements in X-ray technology which allow the analytical spectroscopist to achieve routine high precision in X-ray fluorescence analysis. This statement applies

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not only to "typical" analytical problems (i.e., analysis of relatively heavy elements in solid specimens) but also to less usual situations such as the analysis of elements of relatively low atomic number in liquid matrices. The X-ray method used in the research described herein reveals the total concentration of the element of interest (in this case, sulfur) contained in the sample, without discrimination between oxidation states. The main objective of this research is to demonstrate that the X-ray method can be applied to the analysis of sulfur in various aqueous samples, obtained synthetically or from natural sources. The samples were handled with a minimum of pretreatment or alteration and excellent analytical precision was obtained. The analytical results were compared with those obtained by the classical gravimetric barium sulfate precipitation scheme of analysis which is one of the most accurate methods of sulfur determination.[1] This method has been applied successfully to seawater analysis[2] and has been suggested as the gravimetric method of choice for sulfate analysis in mixtures corresponding to seawater in mineralogical composition.[3]

Sulfur occurs mainly as sulfate in well-oxygenated natural aqueous systems. Under anaerobic conditions, sulfur can be reduced to sulfide which, upon continued exposure to oxygen, may be oxidized to sulfite, thiosulfate, elemental sulfur, and various organically-bound species. An estimation of total sulfur by traditional wet chemical analysis[4] may involve several steps, including removal and determination of sulfides, precepitation of sulfate, and iodometric determination of sulfites and thiosulfates.

Sulfur was chosen as the analyte in this study because of its occurrence in a variety of types of natural waters, its importance as a constituent of seawater, and because of the interesting problems posed by X-ray spectroscopic analysis of sulfur in aqueous mixtures containing large quantities of ions of relatively light elements. Also, the relatively long wavelength of S Kα emission (5.372 Å) makes the X-ray method of analysis potentially susceptible to interferences from the effects of undisclosed macro- and microscopic solid material suspended in the mixture. Gross sample inhomogeneities may also take the form of bubbles, which have a tendency to form from dissolved gases during exposure of the sample to the primary X-ray beam. In the long wavelength region bubble formation can have serious effects upon the analytical results. These analytical factors were evaluated carefully in this study. Natural seawater samples were especially useful in this case because seawater is rich in dissolved gases and suspended material.

METHODS AND MATERIALS

Synthetic solutions were prepared according to the recipe shown in Table I. Standards of variable sulfur concentration (750 to 1050 ppm) were produced by varying the quantity of sodium sulfate added to the basic mixture. Natural seawater samples were obtained by surface sampling at various sites on the islands of Oahu and Kauai, Hawaii. These were spiked with variable quantities of reagent-grade sodium sulfite to produce altered, or "polluted," seawater samples, i.e., solutions which resembled seawater in which a portion of the total sulfur was in a reduced form. Synthetic solutions and natural seawater samples were stored in polyethylene containers which were pretreated to desorb any adhering foreign ions from the container walls. In the initial phase of the study natural seawater specimens were filtered prior to use with Millipore HA 0.45-micron white 47-mm diameter filters.

TABLE I

Recipe for one liter of synthetic seawater

Elements added	Compound used	Amount used (g/l)	Resulting concentrations (ppm)
Mg, Cl	$MgCl_2.6H_2O$	11.2885	1350 Mg; 3937 Cl
Ca, Cl	$CaCl_2.2H_2O$	1.4675	400 Ca ; 708 Cl
K, Cl	KCl	0.7246	380 K ; 345 Cl
Na, Cl	NaCl	23.0932	1900 Cl ; 9083 Na
Na, S	Na_2SO_4	3.9200	885 S ; 1269 Na

The method of gravimetric analysis follows the procedure of Thompson *et al.*[2] All natural seawater samples were analyzed for their sulfate content. In addition, synthetic seawater samples containing 850, 885, and 900 ppm sulfate, respectively, were analyzed by the same method as a check on the accuracy of the precipitation analysis.

X-ray analyses were carried out using a Norelco Universal Vacuum Spectrograph, model 52530, with a thin-window chromium target tube operated at 45 kV and 20 mA. A sodium chloride crystal (2d = 5.639 Å) was used in conjunction with a gas flow proportional counter (e.h.t. = 1.650 kV; p-10 gas) to measure the intensity of S Kα emission at a wavelength of 5.372 Å. A helium atmosphere and coarse collimation were used to maximize measured intensity. Electronic discrimination was employed to reduce noise background. Analytical working curves for the X-ray method were established by using the synthetic sulfate standards described above. Sulfate concentration was plotted versus the measured intensity of S Kα radiation. In order to test the usefulness of the X-ray technique for analysis of seawater specimens of widely varying salinity, the scattered radiation technique[5] was used. The sulfate concentration was plotted versus the ratio of intensities of

S Kα fluorescence divided by the intensity of the scattered continuum at 5.299 Å. In all cases of X-ray intensity measurements, at least 10,000 counts were accumulated.

RESULTS

Replicate gravimetric analyses of the synthetic sulfate standards established the precision of the method. The average relative error in these cases was 0.6%. The maximum range of variation for triplicate analyses on three standards (850, 885, and 900 ppm) averaged about 9 ppm. These results were considered to represent satisfactory accuracy and precision for the gravimetric analyses.

Natural seawater samples collected under aerobic conditions were analyzed by the gravimetric and X-ray methods. The results are shown in Table II. The effect of sample filtration upon the results of the X-ray analyses was investigated. In all cases no statistical difference was found between the analyses of the filtered and unfiltered samples. The X-ray and gravimetric methods agreed to within 2% at the 95% confidence level.

TABLE II

Results of sulfate analyses of natural seawater by X-ray and gravimetric methods

Specimen analyzed	Gravimetric sulfur (ppm)	X-ray sulfur (filtered, ppm)	X-ray sulfur (unfiltered, ppm)
Hanauma Bay I, Oahu	924 ± 6	919 ± 9	923 ± 9
Hanauma Bay II, Oahu	919 ± 6	915 ± 9	913 ± 9
Kokokahi Pier, Oahu	874 ± 5	879 ± 9	886 ± 9
Haleiwa Beach, Oahu	908 ± 6	902 ± 9	901 ± 9
Waimea Bay, Oahu	913 ± 6	909 ± 9	904 ± 9
Lumahai Beach, Kauai	904 ± 6	913 ± 9	920 ± 9

The effect of bubble formation within the sample cell was observed. Measured intensities of the *S* Kα peak were correlated with the appearance of bubbles on the mylar window of the sample cell. No statistically significant change in *S* Kα intensity due to bubble formation was detectable over the relatively short counting time required.

When the salinity of the standard solutions was varied by adding variable quantities of sodium chloride to the basic synthetic seawater recipe, the intensity of the *S* Kα measured from these solutions varied according to the well-known matrix effect.[6] A series of solutions containing identical concentrations of sulfur (885 ppm) but containing widely varying concentrations of sodium chloride was prepared and analyzed according to the calibration curve derived earlier, i.e., in which the sulfur concentration was plotted versus the observed intensity of the *S* Kα radiation. The apparent sulfur values ranged from 891 ppm to 824 ppm, corresponding to sodium chloride concentrations ranging from 3,226 ppm to 41,985 ppm, respectively.

The scattered radiation method of Andermann and Kemp[5] was tested to determine whether the matrix effects resulting from large variations in sample composition could be overcome without resorting to cumbersome indirect methods. The analytical scheme was changed slightly, whereby the intensity of the scattered continuum at 5.299 Å was measured for each sample, as well as the intensity of *S* Kα radiation. The ratio of fluorescent to scattered radiation was computed, and this parameter was plotted versur sulfur concentration. The apparent range of sulfur values was 878 ppm to 868 ppm for the specimens containing 3,266 ppm to 41,985 ppm sodium chloride, respectively.

The apparent correction for matrix effects achieved by the method described above was analyzed in greater detail by means of a further set of experiments designed to separate matrix absorption and enhancement effects.[7] The results of the experiments were interpreted to show that the matrix effect compensation achieved by the scattered radiation method of Andermann and Kemp[5] arises, in this case, as a result of a fortuitous combination of matrix effects which obtains because of the unique character of seawater.

Another study was carried out to determine the effect of the presence of sulfur in reduced forms (in this case, as sulfite) upon the results of the gravimetric and X-ray methods of analysis. Three natural seawater samples collected under aerobic conditions and previously analyzed by the gravimetric method were spiked with measured quantities of reagent-grade sulfate-free sodium sulfite. The samples were then subjected to gravimetric and X-ray fluorescence analysis. Identical gravimetric sulfate values were obtained for the spiked samples; the additional sulfite went undetected by the gravimetric technique. X-ray analysis of these samples gave total sulfur concentrations in good agreement (Table III) with the total of gravimetric sulfate and added sulfite concentrations. Since the samples were of virtually identical salinities, the scattered radiation method was not employed in this case.

CONCLUSIONS

This research has reconfirmed the accuracy and precision of the barium sulfate precipitation method of sulfate analysis in filtered seawater. Sulfur as sulfite is undetected under the chemical conditions used for the gravimetric method. The amount of sample treatment (filtration, precipitation, collection

TABLE III

Results of sulfate analyses of natural seawater spiked with sodium sulfite by X-ray and gravimetric methods

Seawater sample	Waimea Bay, Oahu	Haleiwa Beach, Oahu	Kokokahi Pier, Oahu
Sulfur as sulfate (ppm) (gravimetric)	913	908	874
Sulfite added (ppm)	100.0	200.0	75.0
Gravimetric sulfate and added sulfite (ppm)	1013	1108	949
Total sulfur (ppm) (X-ray)	1018	1113	950
% Difference	0.5	0.5	0.1

and weighing of precipitate, etc.) makes the precipitation method time-consuming and cumbersome, and also completely destroys the seawater sample under analysis.

The X-ray fluorescence method can be applied to the analysis of total sulfur in seawater with a minimum of sample treatment. The sample need not be filtered, and hence is completely unaltered by the X-ray analysis. The scattered radiation method of matrix effect compensation can be applied successfully to the analysis of samples of widely varying salinity because of the cancellation of absorption and enhancement effects.

Within the limits imposed by the inherent precision of the two methods, the results can be compared to deduce the amount of reduced sulfur present in a given sample. The foregoing suggestion is useful in a practical sense, of course, only in cases in which the reduced species is not amenable to identification, isolation, or direct determination.

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