Analysis of the Essential Nutrient Strontium in Marine Aquariums by Atomic Absorption Spectroscopy

An Undergraduate Analytical Chemistry Laboratory Exercise

Laurent D. Gilles de Pelichy, Carl Adams, and Eugene T. Smith*
Department of Chemistry, Florida Institute of Technology, Melbourne, FL 32901-6988

It has been pointed out in this *Journal* (*1*), as well as in other journals (*2*), that the use of real-life samples for unknowns in analytical chemistry laboratory courses greatly increases student interest and curiosity. While a number of excellent laboratory exercises for atomic absorption spectroscopy (AAS) have appeared in this *Journal* over the past decade (*3–9*), only a couple of these articles entailed the analysis of real-life samples (*4, 8, 9*). We present herein an additional interesting undergraduate AAS laboratory experiment involving analysis of the essential nutrient strontium in a real-life sample, sea water.

Marine aquarium hobbyists are very interested in the quantitative analysis of strontium in sea water. Many marine species remove strontium and calcium from sea water to help strengthen their bones, teeth, shells, tissue, or skeletons (*10*). Notably, strontium has similar chemical properties as calcium, and it is just below calcium in the periodic table. It is generally believed that strontium is extracted by biochemical processes in reef tank systems, and that this element needs to be supplemented in tanks containing species that require strontium for optimal growth, especially soft corals. Obviously, depletion of strontium from sea water in a marine aquarium will depend on a number of factors, including the type and amount of various marine species.

The quantitative analysis of strontium in sea water is a problem well suited for an undergraduate analytical chemistry laboratory. The natural abundance of strontium in sea water (7.9 ppm at 35.0% salinity, ref *11*) is well within the detection limit for AAS. Most other trace elements in sea water require a preconcentration step prior to analysis by this spectroscopic method (*9*). Other elements that are in sufficiently high concentrations for direct analysis by AAS (e.g., calcium and magnesium) are more conveniently analyzed by simple colorimetric titrations. Unfortunately, since there are no commercially available colorimetric tests for strontium, most marine aquarium hobbyists follow a prescribed dosage of this element based on time and tank size. In the absence of any test kit, all the local pet shops that have been contacted in our area have expressed great interest in quantitating the levels of strontium by AAS in their soft coral–containing aquariums.

Another advantage to the use of sea water as an analyte is that it contains numerous other components that prevent the direct quantitative determination of strontium as an analyte. Students learn firsthand about the role of interferences in analytical measurements, and about methods to minimize these effects. An important aspect of this laboratory is for students to observe the effect and to take into account interferences in their analysis. This laboratory exercise introduces undergraduates to practical problems associated with AAS.

In addition to providing an excellent learning experience, this laboratory provides a link between commercial interests and academic pursuits. We encourage students as a part of this experiment to collect and analyze marine water samples from local pet shops in addition to a sample from a salt-water aquarium maintained in the hallway of our chemistry department. Students are then responsible for devising a protocol for standard solution preparation, data collection and analysis. Thus, this laboratory exercise clearly represents a practical problem in that both students and pet-store owners find informative.

Experimental Procedure

Marine water samples that were supplemented with strontium from four different soft coral–containing marine aquariums were collected from local pet shops. An additional marine water sample that was not supplemented with strontium was collected from a marine aquarium maintained by the chemistry department. The water from this aquarium originated from the Atlantic ocean. Atomic absorption measurements of water samples were recorded in triplicate utilizing a single-beam Varian SpectrAA 20 spectrometer with an air/acetylene flame and fitted with a strontium hollow-cathode lamp. All concentrations of strontium reported in this study have been normalized for a salinity of 35% (see ref *11*), which was determined from the refractive index of the sample.

Interferences

An important aspect of this laboratory is that the students develop a protocol for the analysis of strontium, which minimizes or accounts for the effects of interferences that diminish the sensitivity for the analyte. Most sources of chemical and spectroscopic interferences are described in detail in AAS textbooks (e.g., *12*). These sources include the formation of oxides and hydroxides in the flame, formation of other low volatile compounds, ionization of analyte, and spectral interferences due to the energy exchange between different types of atoms. For example, the formation of other low volatile compounds (e.g., phosphates and sulfates), as well as other matrix components, is known to diminish the sensitivity to strontium by AAS (*12–15*). A number of methods for the control or elimination of interferences have been employed for AAS (*12*), and two common methods (the technique of standard addition and the use of a releasing agent) that we utilized for the analysis of strontium in marine water are described below.

---

*Corresponding author: Eugene T. Smith, Department of Chemistry, Florida Institute of Technology, 150 West University Boulevard, Melbourne, FL 32901-6988 (phone: 407/768-8000 ext. 7310; fax: 407/984-8461; email: *smithg@fit.edu.*

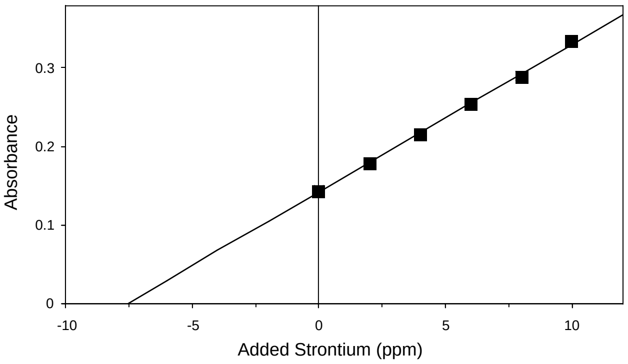

Figure 1. Absorbance versus concentration of a marine water sample containing a known amount of added strontium standard solution. The absolute value of the *x*-intercept represents initial concentration of strontium in the water sample before correction for dilution.

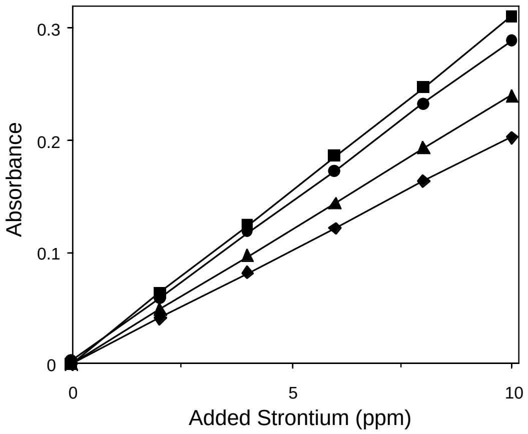

Figure 2. Absorbance vs. concentration of strontium added to distilled water (■), 10.5 ppt sodium chloride (•), 1% lanthanum oxide (▲), and 10.5 ppt sodium chloride and 1% lanthanum oxide (◆) .

Standard Addition. Samples were first analyzed according to the technique of standard addition in order to account for interferences (e.g., see ref *16*). This method is particularly well suited for the analysis of sea water. By adding a concentrated standard solution to the sample, the composition of the solution matrix is not significantly altered. It is assumed that the solution matrix has the same effect on the added standard as it has on the analyte. Thus, the initial concentration of the analyte in the sample is determined by extrapolating the absorbance versus added standard concentration to zero absorbance, and accounting for sample dilution from the addition of the standard solution. In this example, 0.50 mL of various known concentrations of a standard strontium solution (Fischer Scientific, Atlanta, GA) was diluted to 50.00 mL with sea water. The most useful range of standard additions should increase the analytical signal to about twice the original value of the sample. Students are required as a part of the laboratory to develop a protocol for the standard addition method.

Calibration Curves, and Use of a Releasing Agent. Releasing agents are often used in AAS to diminish the effects of chemical interferences (e.g., see ref *12*). For example, lanthanum is commonly used as a releasing agent in the analysis of alkaline earth elements (*4, 12, 14, 17*). In principle, through a competitive equilibrium, this metal will preferentially form complexes with the chemical interferents (e.g. aluminum, phosphate, and sulfate) thus allowing for the elemental analysis of strontium in the flame. If strontium forms complexes, it is less likely to be reduced to the ground state and is therefore unavailable for analysis by AAS. In this exercise, calibration curves were generated for various solutions containing a strontium standard diluted from 0 to 10 ppm, as well as with solutions containing lanthanum oxide (see Fig. 2). The solutions used to generate calibration curves were composed of the following: (i) distilled water, (ii) distilled water and sodium chloride at concentrations similar to that in sea water (10.5 ppt), (iii) distilled water and 1% lanthanum oxide, and (iv) distilled water, 10.5 ppt sodium chloride, and 1% lanthanum oxide.

We chose to analyze a solution containing sodium chloride at concentrations similar to that of sea water simply to observe how the sample matrix influences sensitivity. Other salts may also be used to illustrate this point, including salts that are known to form low volatile strontium complexes (e.g. phosphate and sulfate [*14*]). Due to the complex nature of sea water, we did not make strontium deficient synthetic sea water. It is quite probable that this sample would also result in a matrix that decreases the sensitivity to strontium, but preparation of such a sample would be time consuming, and it is unlikely that it would provide any additional information to the students as to the exact nature of the chemical interferent(s).

Results and Discussion

Standard Addition

We accounted for chemical interferences through the technique of standard addition, and the results are illustrated in Figure 1. In this method, a known but variable concentration of analyte is added to separate aliquots of the sample. The concentration of strontium added to the sample is plotted versus absorbance. As discussed above, it is assumed that the added standard solution interacts with the matrix in a similar fashion as the strontium in the sample. The original concentration of strontium in the sample is determined from the absolute value of the *x*-intercept as illustrated in Figure 1, and after dilution of the sample by the standard solution is taken into account. The concentration of strontium in an aquarium water sample obtained by a standard addition method (7.6 ppm) was in good agreement with reported values for sea water (7.9 ppm, ref *11*). Although our results were slightly lower than previously published values, oceanic concentrations of strontium are known to vary (*10, 11*).

We also tested four samples from pet shop marine aquariums by the standard addition method. After correcting for differences in salinity (*11*), we determined that the concentrations of strontium in all the pet shop tanks (10.5, 10.6, 14.6, and 15.9) were well above the value of 7.9 ppm previously reported for strontium in sea water (*11*). The concentration of strontium was lowest in a marine aquarium sample from our chemistry department (7.6 ppm), which originated from the Atlantic ocean and was not supplemented with strontium.

Releasing Agent

In comparison, the concentrations of strontium in marine water samples from the chemistry department aquarium were all determined to be below 5 ppm by direct analysis utilizing the calibration curves illustrated in Figure 2. The calibration curve used and the strontium concentration detected were as follows: (i) distilled water, 4.6 ppm Sr; (ii) distilled water and 10.5 ppt sodium chloride, 4.2 ppm Sr; (iii) distilled water and 1% lanthanum oxide, 4.1 ppm Sr; and (iv) distilled water, 10.5 ppt sodium chloride, and 1% lanthanum oxide, 3.8 ppm Sr. All these results for the same aquarium sample were significantly lower than the value obtained by standard addition, presumably because interferences were not sufficiently taken into account. Although negative results are obtained from this exercise, a number of good questions are posed to the students, such as, by what mechanism can a sodium chloride solution further diminish the sensitivity to analyte, and why is the releasing agent ineffective? Other possible sources of interferences, which are unaffected by the releasing agent, are listed in the Experimental Procedure section. Students should rationalize the possible role of each source of interference on the sensitivity.

Interestingly, the sensitivities of all the calibration curves illustrated in Figure 2 are about the same, despite the differences in the solution matrix. Figure 2 also illustrates that no enhanced sensitivity to strontium by AAS was achieved through the addition of a releasing agent, 1% lanthanum oxide. Lanthanum, which is commonly used in AAS as a releasing agent for alkaline earth elements (*4, 12, 14, 17*), has been shown to be ineffective when the interfering species—for example, sulfate and phosphate—are present in high concentrations (*14*). Two important lessons to be learned and observed by students from this exercise are that the sample matrix influences sensitivity, and releasing agents are not always effective.

The slightly diminished sensitivity observed for the solutions containing lanthanum oxide relative to the other calibration curves is likely attributed to the flame burner position. The effectiveness of a releasing agent is highly dependent on flame temperature (*17*), which is determined in part by the burner position. For the calibration curves illustrated in Figure 2, the position of the burner was optimized for the solutions containing distilled water, and this position was kept constant for all samples tested. Thus, these calibration curves represent experimental results obtained at essentially the same flame temperature. We have observed that the sensitivity of the calibration curve was dependent on the burner position, but optimizing the burner height for the solutions containing lanthanum oxide did not significantly alter the concentration of strontium detected in the aquarium water sample.

Another AAS method for the analysis of strontium not investigated in this study involves the use of nitrous oxide as an oxidant instead of air. The higher temperatures of this flame enhance the rate of decomposition and volatilization of strontium compounds, thereby reducing the effects of chemical interferences. However, the loss of neutral atoms to ionization of strontium is considerable at these higher temperatures, and it is necessary to add an ionization suppressor (e.g., potassium nitrate or chloride) (*12, 15*). Although not reported in this study, a laboratory for the analysis of strontium utilizing a nitrous oxide–acetylene flame could also be developed. Sea water contains high levels of sodium and potassium, which supply a rich source of electrons to the flame, and thus ionization of strontium should not be a problem.

Conclusion

The quantitative analysis of strontium by AAS utilizing an air–acetylene flame is a challenging and practical exercise for undergraduates. This laboratory is easily incorporated into an analytical chemistry laboratory curriculum and represents an interesting real-life analytical problem. Students learn about an important analytical technique, as well as problems associated with chemical analysis. An additional desirable feature of this exercise is that students are encouraged to interact with commercial enterprises on an applied analytical problem.

Acknowledgments

The assistance of Tanya Bumstead in preliminary studies is gratefully acknowledged. Support for this study was supplied by an institutional grant from Florida Tech.

Literature Cited

1. Sherren, A. T. *J. Chem. Educ.* **1991,** *68*, 598–599.
2. Hughes, K. D. *Anal. Chem.* **1993,** *65*, 883A–889A.
3. Keiber, R. J.; Jones, S. B. *J. Chem. Educ.* **1994,** *71*, A218–A222.
4. Quigley, M. N. *J. Chem. Educ.* **1994,** *71*, 800.
5. Williamson, M. A. *J. Chem. Educ.* **1989,** *66*, 261–263.
6. Sansila, S.; Labinaz, G.; Poland, J. S.; van Loon, G. W. *J. Chem. Educ.* **1989,** *66*, 351–353.
7. Choi, S.; Larrabee, J. A. *J. Chem. Educ.* **1989,** *66*, 864–865.
8. Bye, R. *J. Chem. Educ.* **1987,** *64*, 188.
9. Quigley, M. N.; Vernon, F. *J. Chem. Educ.* **1996,** *73*, 671–675.
10. Riddle, D. *Freshwater Marine Aquarium* **1994,** *17*, 66–76.
11. Riley, J. P.; Skirrow, G. *Chemical Oceanography*; Academic: London, 1965; Vol. 1.
12. Dean, J. A.; Rains, T. C. *Flame Emission and Atomic Absorption Spectrometry*; Dekker: New York, 1975; Vol. 3.
13. David, D. J. *Nature* **1960,** *187*, 1109.
14. Adams, P. B.; Passmore, W. O. *Anal. Chem.* **1966**, *38*, 630–633.
15. Bowman, J. A.; Willis, J. B. *Anal. Chem.* **1967,** *39*, 1210–1216.
16. Harris, D. C. *Quantitative Chemical Analysis*, 4th ed.; Freeman: New York, 1995; pp 139–142.
17. Hoskins, J. W.; Snell, N. B.; Sturman, B. T. *J. Chem. Educ.* **1977,** *54*, 128–130.