The Analysis of Seawater: A Laboratory-Centered Learning Project in General Chemistry

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In 1995 we began modifying the first-year chemistry course at the University of Redlands to accomplish three main goals: (1) to design a curriculum that encourages students to think and act more independently, (2) to lay a foundation for building and maintaining a faculty–student community, and (3) to make the course more interesting by presenting it in an environmental context. In the first semester, the lectures are team-taught to acquaint students with several faculty; students are also introduced to the style of working in groups in a laboratory-centered learning environment that will be reinforced and continued in the second semester.

The seawater-analysis project is designed to introduce students to working in groups; they must collaborate with their colleagues to complete the lab work and assemble the report detailing their findings. Although we want students to be able to design their own experiments as well, we realize this is too much for students to assimilate at once; experimental design is therefore delayed until second semester. This experiment includes qualitative analysis for cations and anions as well as their quantitative analysis by a variety of gravimetric, volumetric, and instrumental methods. Not every student does every experiment; the members of the group are responsible for coordinating efforts to complete all laboratory tasks.

This lab experiment is used to introduce students to the topics of qualitative and quantitative analysis methods, in the context of an overall analysis of an environmental sample. This experiment introduces students to the laboratory methods of gravimetric analysis, potentiometric titration, ion-selective electrodes, and the use of calibration curves to quantitatively determine amounts of metals via the use of atomic absorption and atomic emission. In addition, the students' abilities to perform calculations using unit conversions, dilutions, and molarity are reinforced.

The analysis of seawater has been a rich field for chemical education. Articles have been published in this *Journal* related to the analysis of seawater including measurement of pH and alkalinity and modeling of chemical processes in seawater aquaria *(1),* determination of trace heavy metal ion concentrations *(2),* determination of calcium using ^{45}Ca as a radiotracer *(3),* and general discussions of analytical chemistry in oceanography *(4, 5).* Other articles describe analysis of hydrogen sulfide and acid-soluble metallic sulfides in seafloor sediments *(6),* determination of iodide in seaweed *(7),* chemical reactions and the composition of seawater *(8–10),* 18th century analyses of Dead Sea water *(11),* inorganic nutrients in seawater *(12),* calcium carbonate equilibria *(13),* marine natural products *(14, 15),* and vital materials from seawater *(16).*

Four cations (Na^+, Mg^{2+}, Ca^{2+}, and K^+) and two anions (Cl^- and SO_4^{2-}) comprise greater than 99% of the ionic constituents of seawater. The concentrations of the major ions

Table 1. Ionic Composition of Saline Waters

Ion	Pacific Ocean Water Concentrations / mg L^{-1}		Salton Sea Water Concentrations / mg L^{-1}		Analytical Method
	CRC values [a]	Student Results [b]	Literature Results[c]	Student Results [b]	
Na^+	1.05×10^4	$0.95 \pm 0.13 \times 10^4$ ($n = 7$)	1.24×10^4	$1.27 \pm 0.17 \times 10^4$ ($n = 7$)	Flame emission
K^+	3.80×10^2	$4.2 \pm 0.5 \times 10^2$ ($n = 8$)	—	$3.3 \pm 0.8 \times 10^2$ ($n = 7$)	Flame emission
Mg^{2+}	1.35×10^3	$1.35 \pm 0.19 \times 10^3$ ($n = 7$)	1.38×10^3	$1.31 \pm 0.27 \times 10^3$ ($n = 9$)	Flame absorption
Ca^{2+}	4.00×10^2	$3.1 \pm 0.8 \times 10^2$ ($n = 5$)	1.01×10^3	$0.97 \pm 0.23 \times 10^3$ ($n = 5$)	Flame absorption
Cl^-	1.90×10^4	$1.84 \pm 0.08 \times 10^4$ ($n = 6$)	1.63×10^4	$1.97 \pm 0.29 \times 10^4$ ($n = 12$)	Potentiometric titration
Cl^-	1.90×10^4	$1.87 \pm 0.24 \times 10^4$ ($n = 18$)	1.63×10^4	$1.87 \pm 0.19 \times 10^4$ ($n = 15$)	Single-tube gravimetric
(SO_4^{2-}) [d]	2.65×10^3	$2.3 \pm 0.7 \times 10^3$ ($n = 12$)	1.12×10^4	$1.15 \pm 0.06 \times 10^4$ ($n = 6$)	Single-tube gravimetric
Br^-	6.5×10^1	$8 \pm 2 \times 10^1$ ($n = 3$)	—	$2.0 \pm 0.7 \times 10^2$ ($n = 8$)	Ion-selective electrode

[a]CRC Handbook of Chemistry and Physics, 61st ed.; 1990–91, p 14–10.
[b]Uncertainties expressed as ± one standard deviation.
[c]1999 values *(24);* student analyses performed in 1999 and 2000.
[d]Sulfur exists mainly as sulfate in seawater; sulfide species exist only in trace amounts, except in sediments and anoxic waters.

in ocean surface waters can vary as much as 10%, but their relative proportions remain nearly constant *(8, 17)*. Although the main goal of the seawater project is not precision analysis, it is feasible for general chemistry students to make a proximate total analysis of seawater that is in reasonable agreement with the values shown in Table 1. It should be noted that the students' ability to obtain reasonable data is far greater than their ability to process that data correctly. If authentic seawater samples are not available, artificial seawater can be prepared *(1, 2, 18, 19)*. A recipe is provided in the supplemental material.[W]

Before beginning the seawater project, students are asked to consult the *CRC Handbook of Chemistry and Physics (20a)* to obtain the elemental composition of seawater and to prepare a table of the concentrations, in mg L^{-1} and mmol L^{-1}, of the twenty most abundant elements. Students have access to a computer lab with word processing and spreadsheet software and are encouraged to use a spreadsheet for the table. It is interesting to explore in discussion the resemblance between the electrolyte composition of body fluids and seawater *(21)*, the geochemistry and cosmic abundance of the elements *(22)*, and the question of why some of the nonmetal elements are present as oxyanions, mainly in the highest oxidation state of the nonmetal. For example, sulfur is present mainly not as elemental sulfur or sulfide ion, but as sulfate ion, carbon as bicarbonate ion (considering the pH of seawater), and nitrogen as nitrate ion, et cetera. This can be rationalized by noting that the Earth's atmosphere is an oxidizing atmosphere.

Table 2. Seawater Analysis Project Schedule

Week	Lab Activity Options
0	Pre-lab: Preparation of table of element concentrations in seawater
1	Qualitative analysis for cations in seawater
	Qualitative analysis for anions in seawater
2	Gravimetric analysis for chloride as AgCl
	Gravimetric analysis for sulfate as $BaSO_4$
3[a]	Chloride by potentiometric titration with $AgNO_3$
	Ca and Mg by titration with EDTA using calmagite indicator
	Ca by titration with EDTA using calcon indicator
	Turbidimetric determination of sulfate as $BaSO_4$
	Ca by atomic absorption (flame absorption)
	Mg by atomic absorption (flame absorption)
	Na by flame emission
	K by flame emission
	Br by ion-selective electrode

[a]Detailed procedures are available as supplemental material.[W]

Lab Summary

Three weeks are allotted for the seawater analysis project, including one 3-h lab period per week and some portion of the class time. Table 2 shows the general schedule. Students purchase laboratory experiment "separates" for qualitative cation and anion analysis *(23)*. They are provided with instructions for a simple one-tube gravimetric analysis for chloride or sulfate ions and a titration or instrumental analysis procedure. Student groups can either choose or be assigned which gravimetric analysis and which instrumental analysis procedure to perform. We try to ensure that about half of the overall class does each gravimetric analysis and that about a quarter of the overall class performs each of the instrumental methods.

In the first week of the project, each group begins a qualitative analysis for cations (Ba^{2+}, Na^+, Ca^{2+}, K^+, NH_4^+) and anions (S^{2-}, SO_4^{2-}, SO_3^{2-}, CO_3^{2-}, Cl^-, PO_4^{3-}, NO_3^-) in seawater. Before the end of the experiment, the groups complete these qualitative tests. Students should easily find evidence of five of the six most abundant ions (Na^+, Ca^{2+}, K^+, SO_4^{2-}, Cl^-)[2]; groups are divided upon whether tests indicate the presence of NH_4^+, CO_3^{2-}, and NO_3^-, whose concentrations are at the detection limits for these tests. Student data are summarized in Table 3. At the end of each laboratory session, student groups are responsible for reporting the day's findings on posters that are available outside of lab hours. Each group submits weekly rough drafts of the laboratory report, which the lab instructor critiques and returns before the final report is submitted. Students are required to use word processing for the rough drafts and final report.

In the second week, groups perform a one-tube gravimetric analysis for either chloride (total halide) as AgCl or sulfate ion as $BaSO_4$. Before performing the analysis, students are asked to calculate the volumes of the seawater sample and added reagent that should be used to yield 100 mg of solid considering the expected ion concentration, molarity of added reagent, and total capacity of the test tube. This is a challenging task for most students. Prior to performing the experiment, their results are verified by the instructor. The analysis is carried out in quadruplicate so students will have some notion of the uncertainty in the measurements and have a more statistically reliable result.

In the final week each group performs a titration or instrumental analysis (see Table 2, week 3). If atomic absorption–flame emission spectrophotometers are not available, Ca^{2+} and the sum of Mg^{2+} and Ca^{2+} can be quantified by simple titration procedures using EDTA. Ion chromatography or relatively inexpensive ion-selective electrodes also offer an alternative to the use of flame absorption–emission for the determination of sodium, potassium, magnesium, and calcium ions. Although bromide ion is a minor constituent of seawater, we have successfully combined the use of an ion-selective electrode and the method of standard addition for bromide analysis where there is a 600-fold excess of chloride ion. Detailed procedures are available as supplemental material for this project.[W] Beginning students are capable of analyzing absorption or emission data using a calibration curve, or analyzing data from a titration, especially with extra faculty help. However, we do not expect the students to be able to fully comprehend the details of the Nernst equation; we do expect that they can obtain an answer with assistance and then be able to comment on the meaning of the value obtained. Table 1 shows some typical student results for the analysis of seawater.

Recently, we have extended this project to include the analysis of water from the Salton Sea, a large inland body of water about 90 miles from the University of Redlands, whose total salinity is greater than that of seawater and whose ionic composition differs significantly from seawater *(24).* The results are listed in Table 1.

In their final reports, students are also asked to summarize the class averages from student-reported information on the posters and compare these to the *CRC* (*20a*) values. Along with the group report, students are required to submit a written evaluation of their contributions to the group project and an evaluation of the group itself. The final report is read and graded by the instructor; the grade of each group member is based upon the quality of the group report as well as the student's contributions to the project.

Hazards

The laboratory reagents are corrosive and irritating to the skin and especially to the eyes. Goggles should be worn at all times.

Table 3. Student Qualitative Results[a]

Anion or Cation	Pacific Ocean Water		Salton Sea Water	
	Present	Not Present	Present	Not Present
S^{2-}	7	40	2	40
SO_4^{2-}	43	3[b]	42	0
SO_3^{2-}	0	46	5	37
CO_3^{2-}	21	25	18	24
Cl^-	41	5[b]	34	8[b]
PO_4^{3-}	19	25	21	20
NO_3^-	10	35	18	24
Ba^{2+}	7	40	5	37
Ca^{2+}	42	4[b]	39	3[b]
K^+	47	0	42	0
Na^+	46	1[b]	42	0
NH_4^+	24	21	24	15

[a]Initial results as reported by students; data collected over five years.

[b]When results such as these appear in report drafts or on the posters, faculty feedback to students indicates they may want to experimentally verify their results.

Conclusions

In this project-based experiment, general chemistry students learn to work in groups in a laboratory-centered learning environment. Although this experiment is time-intensive for the faculty during the laboratory, having to grade only one report per group of four students is adequate compensation. Students working in groups for the first time sometimes encounter problems; stronger students may resent their grades depending upon the work of their colleagues. Pointing out that they can maintain editorial control of the final report while having weaker students generate the initial drafts alleviates their anxiety. Faculty need to be aware that group dynamic problems may arise; discussing these problems with students and offering helpful suggestions is necessary.

By working on a multi-week project that requires revision of the laboratory report and comparison of accumulated data, students begin to question the results and develop critical thinking skills. Students also learn about time management. In addition, we have found that making students work in groups keeps students engaged; having group members depend upon everyone's contribution to the overall lab report keeps weaker students from becoming disengaged.

The single general chemistry course offered at the University of Redlands is required for all biology, chemistry, and physics majors; the group of students participating in this experiment is the entire general chemistry student population, not a preselected honors group. While the tasks the students are asked to perform are challenging, most groups rise to the assigned tasks. Introducing first-year students to the "big idea" that chemists examine samples both qualitatively and quantitatively intellectually engages a large fraction of our students. Since the students understand that this is how "chemistry in the real world" is done, they work very hard on this ambitious project. In addition, this project challenges even our top students; no longer have they previously seen everything in the course.

[w]Supplemental Material

Notes for the instructor and detailed instructions for students are available in this issue of *JCE Online*.

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Notes

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2. Mg^{2+} should also be easily detectable by students; we have not yet included this qualitative test in the experiment.

Literature Cited

1. Grguric, G. *J. Chem. Educ.* **2000,** *77,* 495.
2. Quigley, M. N.; Vernon, F. *J. Chem. Educ.* **1996,** *73,* 671.
3. Corless, J. T. *J. Chem. Educ.* **1965,** *42,* 421.
4. Cutshall, N. H. *J. Chem. Educ.* **1977,** *54,* 162.
5. Carritt, D. E. *J. Chem. Educ.* **1958,** *35,* 119.
6. Christensen, J. K.; Høyer, B.; Kryger, L.; Pind, N.; Kong, L. S. *J. Chem. Educ.* **1998,** *75,* 1605.
7. Senyk, J. I. *J. Chem. Educ.* **1977,** *54,* 511.
8. Chave, K. B. *J. Chem. Educ.* **1971,** *48,* 148.
9. Kester, D. R. *J. Chem. Educ.* **1972,** *49,* 11.
10. Goldberg, E. D. *J. Chem. Educ.* **1958,** *35,* 116.
11. Nissenbaum, A. *J. Chem. Educ.* **1986,** *63,* 297.
12. VanLandingham, J. W. *J. Chem. Educ.* **1963,** *40,* 272.
13. Morton, S. D.; Lee, G. F. *J. Chem. Educ.* **1968,** *45,* 513.
14. Scheuer, P. J. *J. Chem. Educ.* **1999,** *76,* 1075.
15. Wood, C. G. *J. Chem. Educ.* **1974,** *51,* 449.
16. Lawrence, A. A. *J. Chem. Educ.* **1944,** *21,* 620.
17. Brown, E.; Colling, A.; Park, D.; Phillips, J.; Rothery, D.; Wright, J. *Seawater: Its Composition, Properties and Behavior,* 2nd ed with corrections; Butterworth/Heinemann, The Open University: Milton Keynes, England, 1997.
18. Bidwell, J. P.; Spotte, S. *Artificial Seawaters: Formulas and Methods*; Jones and Bartlett Publishers, Inc.: Boston, 1985.
19. Millero, F. J. *Chemical Oceanography,* 2nd ed.; CRC Press: Boca Raton, FL, 1996; p 67.
20. Lide, David R. *Handbook of Chemistry and Physics,* 81st ed.; CRC Press: Boca Raton, FL, 2000–2001; (a) p 14-14; (b) p 14-12.
21. White, A.; Handler, P.; Smith, E. L. *Principles of Biochemistry,* 5th ed.; McGraw-Hill: New York, 1973; pp 879–882.
22. Dutch, S. I. *J. Chem. Educ.* **1999,** *76,* 356.
23. Postma, J. M.; Roberts, J. L.; Hollenberg, J. L. *Chemistry in the Laboratory,* 5th ed.; Freeman: New York, 2000; experiments 33 and 34.
24. Salton Sea Authority. *http://www.lc.usbr.gov/saltnsea/deistoc.html* pp 3–13 (accessed Nov 2002).