Analytical Problems Associated with the Analysis of Metals in a Simulated Hazardous Waste W

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Background

There have been a number of excellent articles describing guided-inquiry teaching methods for the analysis of metals (*1–5*). Interviews of alumni from numerous undergraduate chemistry programs indicate that these are strongly needed. Students feel that one major void exists in their education: real-life applications of chemistry laboratories. My most vivid memory (horror) of my first job in industry was my lack of training in analyzing problematic samples (industrial waste, hazardous waste, contaminated soil and sediments, and biological samples) and interpreting unclear results. This problem poses a huge dilemma for chemistry professors—how do we teach the fundamental principles of chemical and instrumental theory that must be covered *and* provide the students with real-life applications to prepare them for their careers in industry?

Although inquiry-based learning methods are becoming a common theme in chemistry departments, many faculty members find it hard to continue this educational approach in upper-level classes. The series of laboratory exercises presented here is another attempt to bridge this gap between student needs and desires. While these exercises do not introduce a new analytical technique, they do exemplify a new guided-inquiry approach—project-based learning—to teaching undergraduate instrumental analysis and environmental chemistry.

Most first- and second-year chemistry laboratories rely on what are best described as *clean samples*: students are asked to identify the contents of an unknown sample (distilled water containing one or only a few analytes). This is a necessary evil for these introductory courses, since unclear titration end-points and vague inflection points would only frustrate students and turn them away from a chemistry degree. In upper-level courses, however, unclear titration end-points and samples composed of a complex matrix greatly enhance the educational experience by allowing students to learn advanced sample-handling techniques and challenging their ability to interpret results.

Lab Approach

The focus of this laboratory exercise is the analysis of metals in complex sample matrices by a variety of wet and instrumental techniques. The target courses for this exercise are upper-level instrumental methods of analysis or environmental chemistry. Six techniques are presented here, but they may be used singly or in any combination as time permits. Those who teach voltammetry or inductive coupled plasma emission spectroscopy (ICP) as part of their instrumental course may wish to include these techniques because they complement the instrumental methods presented here.

This laboratory exercise is in its third year of use at Whitman College. It works best when the course has two laboratory meetings per week, which is still common for many instrumental methods of analysis courses. Seven lab periods are allowed for students, in pairs, to complete the procedures described. To avoid bottlenecks at an instrument, labs are scheduled on a rotating basis so that no two students are using an instrument at the same time.

Instructions for six procedures to determine the calcium in a simulated hazardous waste sample are available online.[W] The procedures are (i) flame atomic absorption spectroscopy (FAAS) using external standard calibration, (ii) FAAS using external standard calibration with a releasing agent (Sr), (iii) FAAS using standard addition, (iv) FAAS using standard addition with a releasing agent (Sr), (v) ethylenediaminetetraacetic acid (EDTA) titration, and (vi) Ca-ion-specific electrode. Explicit cookbook details on how to prepare solutions, make dilutions, or give an indication of what Ca concentration to expect in the sample are not given.

An introduction to and overview of the FAAS unit, safety procedures, and the calcium electrode are given at the beginning of the first lab. Calcium is used as a surrogate for a heavy metal to avoid hazardous waste disposal problems. Carbonated beverages are excellent simulated hazardous wastes because they (i) provide a potential physical interference in the FAAS procedure (viscosity); (ii) contain interfering chemical substances such as dissolved gases (which make pipetting difficult if the sample is not first degassed), metals (magnesium), and matrix components (phosphates, which produce a non-dissociating species in the AAS flame); and (iii) pose no health threat to the students. Students are instructed to treat the sample, which they are told is a soda sample, as a toxic, life-threatening hazardous waste. (As added entertainment, instructors can draw the Grim Reaper's scythe on adhesive notes and give them out when poor sample-handling techniques are observed.)

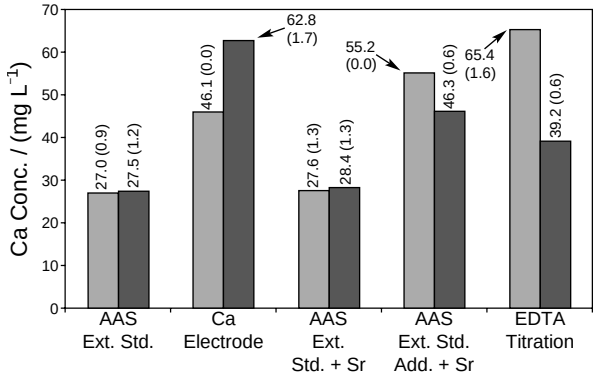

Figure 1. Student data from the analysis of a single simulated hazardous waste sample (Classic Coca-Cola). Results from two groups of students are shown for each technique. The numbers above each bar are the mean Ca concentration of three replicate analyses. The standard deviation is shown in parentheses.

A common problem with laboratories that meet twice a week is how to handle all the lab reports. Students strongly dislike writing a report for each lab and most instructors do not have the time to grade all the reports in sufficient detail. As a capstone exercise for this series of laboratories, students are required to research and write an article suitable for publication in *Analytical Chemistry*. They find this to be one of the most difficult parts of the exercise.

Materials and Supplies

Chemicals

One or more carbonated beverages (Coca-Cola and Pepsi appear to be the most challenging to analyze)

A reference Ca atomic absorption standard (1000 mg/L)

$Sr(NO_3)_2$ salt for use as a releasing agent in the FAAS analysis

Ultra-low AAS-grade concentrated nitric acid and two empty 2-L acid bottles for dilutions

Three liters of standardized $Na_2H_2EDTA{\cdot}2H_2O$ solution (FW = 372.25 g/mol); dry at 80 °C for 1 h, cool, weigh out ca. 0.6 g, and dissolve in 400 mL of deionized water; fill to the mark in a 500-mL volumetric flask; know the exact weight of EDTA to determine the molarity

NaOH solution, 50% by wt

Solid hydroxynaphthol blue as an indicator in the EDTA titration.

Instruments

1 Ca AAS hollow cathode lamp

1 FAAS unit (a Perkin-Elmer 1100B was used in these experiments

1 presoaked Corning Ca electrode and ionic strength adjuster

1 single-junction reference electrode

1 millivoltmeter

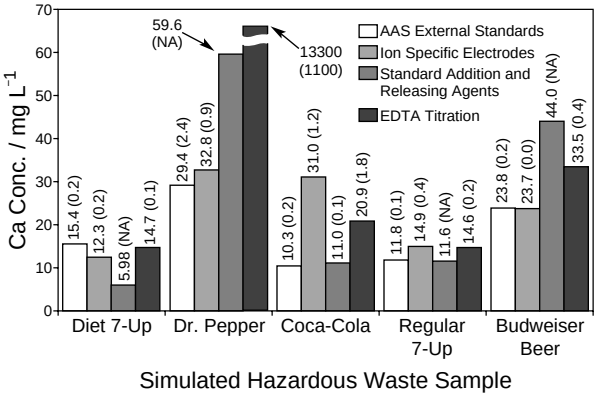

Figure 2. Student data from the analysis of five simulated hazardous waste samples. Each group of students analyzed a different sample by four techniques. The average Ca concentration for 5 replicates is shown above each bar, with the standard deviation in parentheses. No standard deviation is available for the standard addition technique because only one sample was analyzed.

Hazards

Although this experiment presents no unusual hazards, standard precautions should be used in handling acid solutions and disposing of chemical wastes. These experiments were designed to minimize the generation of hazardous wastes by using simulated waste samples and by analyzing for Ca instead of a heavy metal.

Student Evaluations

The first reaction from students is a temporary confusion about where to start. They have a basic procedure, but without knowing the approximate Ca concentration in their sample, they have difficulty selecting a sample dilution to begin with. For procedures involving instruments, it is always suggested that they start with a high dilution of the sample (1- to 10- or 1- to 100-fold) so they do not cross-contaminate their reference standards. For other procedures, such as titrations, students are at first reluctant to start because the dilution may be wrong. "So what, you have to start somewhere. And there is no harm in redoing a titration."

After the first laboratory exercise has been completed the following lab periods go much smoother. However, confusion rapidly spreads through the lab when results from different techniques show significantly different Ca concentrations in the same sample. Results shown in Figure 1 indicate fairly good agreement among groups for the FAAS techniques. However, when the same sample was analyzed by two groups using the EDTA titration and the Ca electrode procedures, very different results were reported. "How can this be?" ask the students. "We carefully followed the procedures." Then we look at how each group approached the task. Different dilutions in the Ca electrode procedure could produce different results, since the effect on the ionic strength adjuster may be different. The most challenging technique is the EDTA titration, perhaps the one the students feel they have the most experience and confidence to conduct. However, the coloring agent in Coca-Cola interferes with the end point of the hydroxynaphthol blue indicator. Students approach this problem in different ways, which include dilution of the sample to remove the color (thus increasing the detection limit), dilution of the standardized EDTA solution, or requesting a smaller buret. Finally, students recall what each technique detects: the FAAS detects total Ca, the Ca electrode detects only Ca^{2+} ions, and the EDTA titration measures all divalent ions that complex EDTA at a pH of 10. The student who does all of these is ready for the real world.

The best application of this laboratory exercise was in a class divided into five groups, each of which was given a different simulated hazardous waste sample. Results from this lab are shown in Figure 2. As the students collected and compared data, minor panic broke out in the lab. As seen in Figure 2, no one procedure consistently produced the highest Ca concentration, which was the presumed "best answer". Also, only the analysis of the regular 7-Up sample produced consistent Ca concentrations. But this was the assignment: determine the *best* procedure for *your* sample! In addition to the analytical problems discussed for the data in Figure 1, the students finally conclude that different samples are subject to different (or no) interferences.

Another difficult part of this exercise is the writing of a manuscript that follows the guidelines of *Analytical Chemistry*. At this point in their academic career, students have usually mastered the art of writing lab reports. However, eliminating the use of first- and second-person pronouns (as some journals require), condensing laboratory procedures to a paragraph, and not publishing calibration curves are difficult concepts for them to master.

Although there are many difficult moments in this set of experiments, the students are more than pleased with their results. This lab is consistently voted the most enjoyable and best learning experience of the labs used in instrumental methods of analysis. More importantly, the students are better prepared to analyze real-world samples upon graduation.

Acknowledgments

I would like to thank the Instrumental Analysis classes from the spring of 1999 and 2000 for collection of the data and patience in the development of this educational exercise. I am also indebted to Fred Girod of the Collegium Budapest–Institute of Advanced Study for the use of computers and Internet services during the preparation of this manuscript.

[W]Supplemental Material

A list of required chemicals and instruments and instructions for all of the procedures are available in this issue of *JCE Online*.

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