Lab Documentation

Chemicals needed for the following procedures:

Instructor Information

Chemicals:

One or more carbonated beverages. Coca-Cola and Pepsi appear to be the most challenging to analyze. Other options that have been tried are 7-Up (diet and regular) and Budweiser beer.

A reference Ca Atomic Absorption standard (1000 mg/L)

$Sr(NO_3)_2$ salt (CAS number 10042-76-9) for use as a releasing agent in the FAAS analysis.

Untra-low AAS-grade concentrated nitric acid (CAS number 7697-37-2) and two empty 2-L acid bottles for dilutions

Three liters of standardized $Na_2H_2EDTA\text{-}2H_2O$ solution (FW=372.25 g/mol, CAS number 6381-92-6) dry at 80^{o}C for 1 hr, cool, weigh out ~0.6 g and dissolve in 400 mL DI. Fill to mark in 500 mL vol. know the exact weight of EDTA for determining the molarity.

50 % by wt NaOH (CAS number 1310-73-2)

Solid hydroxynaphthol blue (CAS number 63451-35-4) as an indicator in the EDTA titration

Instruments:

A Ca AAS hollow cathode lamp

An AAS unit. A Perkin-Elmer 1100B was used in these experiments.

A pre-soaked Ca Electrode and ionic strength adjustor. Corning Model 34120-70 (VWR Scientific Products Catalog Number 34120-706) was used in these experiments.

Reference electrode for the Ca ISE.

A millivolt meter.

Metal Analysis: Ca Determination by A Variety of Techniques

Student Information

The purpose of this series of laboratory exercises is to show that many elements and compounds can be analyzed by more than one technique. Some of these techniques are more direct and simple, while others are more involved. When samples from industry or the real world are analyzed, an additional consideration interferences must be also considered. Many samples contain such complicated interferences that the sample is described as a complex matrix . It should be no surprise, that when a complex matrix is analyzed by a variety of techniques, that the measured concentrations do not always agree. In these labs, you will measure the concentration of Ca in a simulated hazardous waste by flame atomic absorption spectrophotometer (FAAS using external standard and standard addition techniques as well as matrix modifiers), by EDTA titration (an applied review of quantitative analysis), and using a Ca^{2+} ion-specific electrode (another review of quantitative analysis). Although your sample is safe , as you handle it, consider it as a hazardous waste. What steps will you take in the following procedures to protect yourself and your lab partners?

The order that you do these labs is not important and they will be randomly assigned so that no two groups are doing the same lab at the same time. The labs are:

-determination of Ca by flame atomic absorption spectroscopy using external standards without a releasing agent (Sr^{2+})

-determination of Ca by flame atomic absorption spectroscopy using external standards with a releasing agent (Sr^{2+})

-determination of Ca by flame atomic absorption spectroscopy using standard addition without a releasing agent (Sr^{2+})

-determination of Ca by flame atomic absorption spectroscopy using standard addition with a releasing agent (Sr^{2+})

-determination of Ca by EDTA titration

-determination of Ca^{2+} by ion-specific electrode

At the beginning of the first lab you will have to remove the carbonation in your sample by placing it in a vacuum system for at least 1 hour.

**FOR EACH TECHNIQUE (except the standard addition) ANALYZE THE UNKNOWN SAMPLE FIVE TIMES

What do you turn in?

One of the goals of the chemistry department is not only to teach you proper methods for analyzing samples, but to also teach you to how to analyze the data and to effectively disseminate your results and conclusions. One dissemination method is your lab notebooks and lab reports that you will complete for the other labs, but for this lab you will do something a little different. After completion of all experiments, you are to compile the methods and results and write a journal article suitable for publication in the *Journal of Analytical Chemistry*. The theme of your article will be comparing analytical techniques for Ca analysis of complex aqueous samples. You are upper-level students about to impart on the real-world so I will treat you as such. You must obtain the Instructions to Authors for the *Journal* from the library or Internet and follow proper scientific writing guidelines (refer to the *ACS Style Guide* in room 307). Remember that in your lab reports you are to write down meticulous lab methods and show calibration curves, but you will not be able to do this in your journal article (if you did the article would be 50 pages long). You must decide the fine line between too little and too much information. The best way to do this is to review several articles in the *Journal* (perhaps 2 or 3 on AAS, 2 or 3 on titration techniques, and 2 or 3 on ion-specific electrodes). Note that you MUST also do a literature search on your topic and include these results in your introduction. Your article should be no longer than 25 typed double-spaced pages including text, figures, tables, and references. In your discussion and conclusions section, defend which method is the most accurate for determining the Ca concentration in your sample.

Atomic Absorption Spectroscopy

Student Information

Useful References:

Van Loon, J.C. *Analytical Atomic Absorption Spectroscopy:* QD96 .A2V36

Selected Methods

Ebdon, et al. An Introduction to Analytical Spectrometry QD96 .A8 I58 1998

J. Chem. Ed. Index Search (an online searchable database of articles in the *Journal of Chemical Education*

http://jchemed.chem.wise.edu/Journal/Search/index.html

Harris, Daniel C., Quantitative Chemical Analysis, Fifth Edition, 1998, W.H. Freeman.

Skoog, Holler, & Nieman, Principals of Instrumental Analysis, Fifth Edition, Saunders College Publishing, 1998.

Before beginning any experiments that use the AAS, you are expected to learn about the instrument and analytical methods by reading the relevant sections in your textbook. Also some reading will be made available from the instrument manuals.

There are also guidelines for each instrument for startup and shutdown. Follow these closely!

FIVE CARDINAL RULES TO BE FOLLOWED WHEN OPERATING THE INSTRUMENT:

1. ALWAYS wear safety glasses when in the vicinity of the instrument.
2. NEVER leave the flame unattended. Shut it off when you leave the room, even for a few seconds.
3. CONSERVE acetylene shut off the burner when not doing analyses it burns C_2H_2 at the rate of over 4 L/min.
4. DO NOT operate the instrument until you have been checked out by me.
5. Regarding the air and acetylene when using older instruments: ALWAYS TURN THE C_2H_4 ON LAST AND OFF FIRST. TO DO OTHERWISE INVITES A POSSIBLE EXPLOSIVE FLASHBACK.
6. Before you use the AAS, CHECK and make sure the drain tube loop contains water.
7. CHECK to make sure the waste container is not full.

Determination of Ca using Atomic Absorption Spectroscopy using External Standard Addition (with and without Sr^{2+})

Student Procedures

Purpose: (1) refine your ability to make reference standards (Ca^{2+}), (2) learn to use the flame atomic absorption spectroscopy system, (3) determine the linear range for the instrument, and (4) determine the concentration of Ca in a simulated hazardous waste sample (analyze your sample at least 5 times).
Plan ahead, have your calculations make for your solutions, and completely understand this procedure before you come to lab (Reading for the AAS is in Chapters 8 and 9, Skoog).

Exercises:

Prepare all solutions first. When you are approximately 20 minutes from finishing making your solution, turn on the AAS unit, adjust the lamp current, and allow it to warm up (about 20 minutes).

External standard calibration method (without the Sr^{2+} matrix modifier):

This is the normal way of using a calibration curve; you make a set of standards, measure the instruments response to the standards and unknowns, make a plot, and use the instrument response to estimate the concentration. I suggest analyzing your standards from low to high concentration and making a blank measurement between <u>each</u> standard. Repeat this entire process twice. This will give you 15 to 20 blank measurements, which you will need to determine the signal to noise ratio.

- Make a set of Ca standards (in 1 % HNO_3). Concentrations (as Ca) should range from 0.1 to 50 mg/L. Evenly divide up the concentrations into 10 standards. Note that some of these standards will be below the detection limit while others may be above the limit of quantitation (LOQ).
- Make 5 replicate solutions of your simulated hazardous waste sample.
- Set up the AAS as instructed (you should already know the lamp current, wavelength, slit width, and fuel and air flow rates before you arrive in lab).
- Analyze the standards and unknown samples on the AAS.
- Plot the data, approximate the linear portion of the data, and if the unknown sample signal is in the linear range, estimate the concentration of Ca. (You will have to re-do this more accurately for you

report.) If the signal of the sample is too high, make the appropriate dilution of the sample in 1 % HNO_3, and reanalyze all five replicates of your sample.

External standard calibration method (with the Sr^{2+} matrix modifier):

We will also evaluate the affect of adding a releasing agent (Sr). You should completely understand why you are adding this before you come to lab.

Again, I suggest analyzing your standards from low to high concentration and making a blank measurement between each standard. Repeat this entire process twice. This will give you 15 to 20 blank measurements, which you will need to determine the signal to noise ratio.

- Make a stock solution of $Sr(NO_3)$ at a concentration that will serve to meet the requirements below. Check with me before you make the solutions to ensure that you have completed the calculations correctly.
- Make a set of standards and samples containing Sr at a final concentration of 1000 mg/L. Calcium concentrations in the final standards should be 0, 0.5, 1, 5, 10, 15, 25, and 50 mg Ca/L. Also make sure that each standard and sample contains a final concentration of 1% nitric acid. When you make these solutions, I suggest making the samples in 25, 50, or 100 mL volumetric flasks. For example, when preparing a standard in a 25 mL volumetric flask, add a volume of standard to yield the desired final concentration of Ca, a volume of concentrated nitric acid to yield 1% in the final solution, the required volume of Sr solution to obtain 1000 mg Sr/L in the final solution, and fill the remainder with distilled water. For a sample in a 25 mL volumetirc, add an exact and known volume of sample (as much as possible since this will improve your detection limit), concentrated HNO_3 to yield 1% in the final solution, a volume of $SrNO_3$ solution that will give you 1000 mg Sr/L in the final solution, and fill the flask with distilled water to the mark. Remember to make 5 replicate solutions of your sample.
- Set up the AAS as instructed 20 minutes before you are finished making your solutions. You should already know the lamp current, wavelength, slit width, and fuel and air flow rates.
- Analyze the standards and samples on the AAS.
- Make sure that the data set is linear. If it is not, consult me before you throw away your solutions.
- Plot the data, approximate the linear portion of the data, and if the unknown sample signal is in the linear range, estimate the concentration of Ca. (You will have to re-do this more accurately for your

article.) If the signal of the sample is too high, make the appropriate dilution of the sample in 1 % HNO_3, and reanalyze all five replicates.

Determination of Ca using Atomic Absorption Spectroscopy using the Standard Addition Technique (with and without Sr^{2+})

Student Procedures

Purpose: (1) refine your ability to make reference standards (Ca), (2) learn to use the atomic absorption spectroscopy system, (3) learn the standard addition technique, (4) learn one technique for overcoming interferences, (5) determine the concentration of Ca in a simulated hazardous waste sample.

Plan ahead and completely understand the standard addition procedure before you come to lab (Reading for the AAS is in chapters 8 and 9, Skoog, while information on releasing agents and standard addition can be found on pages 221 and 15-18 respectively. With respect to the standard addition method I will show you a better way of doing this. **DO ALL CALCULATIONS FOR DILUTIONS AND PREPARING SOLUTIONS BEFORE YOU COME TO LAB OR YOU WILL BE VERY LATE LEAVING TODAY**

Exercises:

Prepare all solutions first. When you are approximately 20 minutes from finishing making your solution, turn on the AAS unit, adjust the lamp current, and allow it to warm up (about 20 minutes).

Standard addition calibration method with the Sr^{2+} releasing agent:

Here, we are concerned with overcoming viscosity effects from the sample matrix. We ignored this in the external standard method, but it may have been present. We will also evaluate the affect of adding a releasing agent (Sr) to your sample and standards. You should completely understand why you are adding this, before you come to lab.

- Make a stock solution of $Sr(NO_3)$ at a concentration that will serve to meet the requirements below. Check with me before you make the solutions to ensure that you have the calculations correct.
- Make a set of solutions containing a known amount of Ca (standard), your hazardous waste sample, and Sr (at 1000 mg/L in the final solution). As a starting point, calcium concentrations in the final solutions should be 0, 0.5, 1, 5, 10, 15, 25, and 50 mg Ca/L. BUT you must determine the exact range of standards. Review the standard addition procedure in Skoog. Based on your earlier determination of Ca in your sample, add an appropriate range of Ca to your samples to yield a plot similar to the one in your textbook. (For example, you should not have to over-extrapolate your plot to estimate the concentration of Ca in your sample the positive range of your standards should be of the same scale

as the negative extrapolation.) When you make these solutions, I suggest making the samples in 25, 50, or 100 mL volumetric flasks. (For example, if a 25 mL volumetric flasks are used, add 10 mL of your simulated hazardous waste sample, a volume of concentrated nitric acid to yield 1% in the final solution, the required volume of Sr solution to obtain 1000 mg Sr/L, and fill the remainder with distilled water.) (i.e. to each volumetric flask add (1) an exact and equal volume of sample to each flask (as much as possible), (2) concentrated HNO_3 to yield 1%, (3) a volume of $SrNO_3$ solution that will give you 1000 mg Sr/L, and (4) fill the flask with distilled water to the mark.)

- Set up the AAS as instructed 20 minutes before you are finished making your solutions. You should already know the lamp current, wavelength, slit width, and fuel and air flow rates.
- Analyze the solutions on the AAS unit.
- Make sure that the data set is linear. If it is not, consult me before you throw away your solutions.
- Plot the data, determine the linear portion of the data, and if the unknown sample signal is in the linear range, determine the concentration of Ca. (You will have to re-do all of this using your spreadsheet.) If the signal of the sample is too high, make the appropriate dilution of the sample in 1 % HNO_3, and reanalyze all five replicates.

Standard addition calibration method without the Sr^{2+} matrix modifier:

Repeat the procedure given above but do not add Sr^{2+} to your solutions.

AAS Questions for the Students

In the four AAS procedures we are evaluating one physical and one chemical interference. The physical interference can be evaluated by comparing the difference in the detection limit and slope of your calibration curves for each procedure. The chemical interference will be distinguishable with the use of Sr in your samples (and standards). Not all simulated hazardous waste samples will have both interferences. If these are observed for your sample, use them as a point-of-discuss in your article.

In each of the AAS procedures you may have diluted your simulated hazardous sample for analysis (with Sr, HNO_3, etc.). How will you account for this dilution when calculating the concentration of Ca in your original sample?

Exactly what type of Ca does the FAAS technique measure?

What special handling procedures did you develop for:

dermal contact with the sample?

volatile toxins that may be in the sample?

Determination of Ca using the EDTA Titration

Student Procedures

Purpose: (1) develop your ability to perform titrations of complex samples, (2) review/learn the details of the EDTA titration, and (3) determine the concentration of Ca in a simulated hazardous waste sample.

Plan ahead and completely outline a procedure before you come to lab (Reading for the EDTA titration can be found in Harris, 1988 (Chapter 13 in Quantitative Chemical Analysis, 5th edition, W.H. Freeman and Company, NY). A guideline for your experiment can be found in experiment 29-9 (page 853). In procedure 29-9 you will not need to complete the Mg determination (steps 2 and 3) or need the pH 10 buffer or Eriochrome black T indicator. A solution of reference EDTA will be provided to you.

Consider the following when preparing for your laboratory exercise:

What is the color change for the Eriochrome black T indicator?

What problems might a sample with strong color pose in your titration?

How could you overcome this problem while maintaining a low detection limit?

Exactly what type of Ca does the FAAS technique measure?

Determination of Ca using a Ion-Specific Electrodes

Student Procedures

Purpose: (1) refine your ability to make reference standards (Ca) and dilutions, (2) review/learn the details of ion-specific electrodes (3) determine the concentration of Ca in a beverage sample.

Plan ahead and completely outline a procedure before you come to lab (Reading on electrodes can be found in Harris, 1988 (Chapter 15 in Quantitative Chemical Analysis, 5th edition, W.H. Freeman and Company, NY). This should be a review from Quantitative Analysis, although you may not have specifically used a Ca electrode, you should know the basic technique. Consult the user manual operation for operation of the Ca electrode (provided in lab).

Exercises:

Follow the instructions in the electrode manual, but make an external calibration curve to check the slope of the calibration line. If it is within the acceptable range, analyze your sample five times. Estimate the Ca concentration using the linear least squares (LLS) analysis.

Exactly what type of Ca does the FAAS technique measure?