

## CHEM 314: Metals Prelab and Procedure

### Background

There are several ways of performing elemental analysis. In this lab, we will compare the results from an energy dispersive X-ray Fluorescence instrument with Flame Atomic absorption and ICP-MS. Each technique has both advantages and limitations.

The handheld X-ray fluorescence (XRF) spectrometer is an energy dispersive instrument that is a quick, convenient way of determining the elemental composition of a sample. It can yield excellent results for samples like steel with high concentrations of heavy elements. However, due to the attenuation of low energy x-rays in air, it is of limited application for light elements.

Flame Atomic Absorption (Flame AA) is still a workhorse in many analytical laboratories for doing routine analysis of relatively high concentration samples. The Flame AA is relatively simple to run and troubleshoot, but can only analyze for one element at a time. Flame AA also has relatively high detection limits of hundreds of ppb for most elements.

ICP-MS is the current industry standard for trace metals analysis. This instrument requires substantial operator skill, but is capable of very low ppt ( $>0.01$  ppt) detection limits for many elements. Two of the primary concerns with this instrument are contamination- eye makeup and street shoes are not allowed in the ICP-MS room- and dilution error.

In this lab, we will be using the XRF and flame AA to quantify major elements and ICP-MS for trace elements. The prelab questions and procedure below will help you develop an appropriate plan for elemental analysis.

### Safety

This lab requires the use of concentrated nitric acid in order to digest metal in samples. Nitric is a **strong, oxidizing acid** that can cause skin burns (MSDS available on the website). Reactions with metal generate  $\text{NO}_x$  gasses that are toxic and must be kept in the hood (MSDS available on website). To mitigate the chance of exposure, the acid dispensed using a refluxer, in the hood with the sash down and gloves and safety glasses will be worn when handling the acid. After digestion of metal samples, acid must be diluted before being removed from the hood. If accidental exposure occurs, the individual will flush the affected area with water for 20 minutes. Small spills within the hood will be neutralized using calcium bicarbonate, which is kept inside the hood.

### Procedure

1. Take a picture of your product before you start destroying it and maybe take pictures of the component pieces.
2. Dismantle your product into its component pieces
3. Use the handheld XRF to quantify metals in your product. Perform three separate analysis and be sure to record the results of each in your lab notebook. Use saran wrap to isolate messy samples from the instrument.
4. Clean the metal of paint or polymer coatings. Repeat XRF analysis to see if it changes.
5. Record the mass of four beakers and label them.
6. Cut your metal into 4 uniform-ish pieces with individual pieces weighing less than 1.5g. Weigh these pieces and record the results in your lab notebook. Keep track of which sample is which by keeping them in labeled beakers.
7. In the hood, add 5 ml aliquots of concentrated nitric acid to each beaker. Wait 15 minutes. Add additional acid if needed to reach complete dissolution.
8. Add ~25 ml of 18 M $\Omega$  distilled water to each beaker (water available in a carboy, not from the tap). Record the total mass.

9. Filter each sample into a PLASTIC storage container using a syringe and VWR 0.2um polyethersulfone filters and save it until you have good results from ALL analysis.
10. Prepare standards for your calibration curve for Flame AA analysis.
11. Prepare any quality control samples for Flame AA analysis.
12. Dilute your samples for Flame AA.
13. There are instructions for running the Flame AA located near the instrument in REIC 245. Instructors will also be available to assist you. Be sure to consider the order you will run your samples in.
14. ICP-MS samples must be diluted in 2% trace metal free HNO<sub>3</sub>, available from the TA.
15. Submit your samples to the instructor or TA for analysis. Be sure to use very good labeling!

### Annotated Figures and Calculations

Complete annotated figures will include all criteria outlined in the CPCP instructions as well as:

- DO NOT INCLUDE RAW DATA
- Flame AA- Calibration curve with error bars, a line of best fit, and an r-squared value on the plot. Calculate the error associated with the measured concentration of your unknown ( $s_x$ ) and show an example calculation.
- A hand-written example back-calculation from the concentration in solution to the weight percent or parts per million in the original hunk of metal. Be sure to be neat, include units, and pay attention to significant figures. See example instructions on the website. Excel can be used for the bulk of the calculations and the calculation of  $s_x$ .
- Be sure to calculate back all the way to the metal weight percent or parts per million (mg element per kg sample) in the original solid sample you dissolved.
- Take care with your significant figures and include estimates of error for every number.
- A single table of XRF, Flame AA, and ICP-MS results- including estimation of error for all measurements
- Calculate the percent recovery for your sample overall using combine ICP-MS and Flame AA data
- Calculate the percent recovery for your sample overall using handheld XRF data
- Identify the metal in your product

### Discussion points

- Are your results consistent with your expectations- the metals you are expecting in your sample?
- Does your calibration curve seem correct? Is the intercept near zero? Is it linear? Does it have a good r-squared value?
- Comparison of major, minor, and trace metal content by each technique.
  - Do the techniques agree?
  - Are replicate measurements precise?
  - If not, offer a plausible explanation for any discrepancies you identified.
- What is the largest source of error in each experiment? How can it be mitigated?
- How might you change the experiment in the future?

**References-** Available on the metals website.

Thermo Scientific. "AAS, GFAAS, ICP, or ICP-MS? Which Technique should I use? An elementary overview of elemental analysis."

Skoog, D.A.; Holler, F.J.; Nieman, T.A., *Principles of Instrumental Analysis*. Saunders College Publishing: Chicago, **1998**.

**Prelab 1****To be completed before coming to lab on the first day of the Metals Experiment.**

1. What metals are typically in steel and at what concentrations or mass percentages?

List up to 10 elements:

Reference:

2. If your sample is 97% Fe, determine how much your stock solutions need to be diluted to make a 3ppm sample for Flame AA analysis.

3. The linear range of the flame AA is 1-10 ppm. Determine a method to make calibration standards from  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  that are in the appropriate concentration range.

4. Prepare data tables to record the lab work for sample preparation and dilutions for Flame AA analysis. Flame AA results will be printed out at the time of analysis.

