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Dispersive X-Ray Fluorescence Measurement of Trace Zinc Contamination on Lab Benches

Please read the following references: Chapter 10 of Instrumental Analysis by Granger. Chapter 21 in Harris to learn about x-rays fluorescence. Read Chapter 12 in Skoog to learn also about x-rays and the dispersive x-ray fluorescence.

Introduction. Contamination is a big problem in any analysis of trace materials. Small amounts of certain undesirable species can render an experiment or a chemical process worthless. This is particularly true in production of semiconductors but it is also true in environmental analyses or in other laboratory settings where trace analysis is done. It does not take much of a contaminant to render an analysis worthless.

A wipe test is among the most common techniques for contamination control of laboratory surfaces and tools. Usually, the wipes containing the contaminants are digested in acid and analyzed by high sensitivity methods such as inductively coupled plasma mass spectrometry.

We will use a wipe test to measure for contamination of the lab bench surface in the lab by zinc a very common contaminant substance. Instead of acid digestion, we will use a rapid measurement of x-ray fluorescence to identify contaminants and to quantitate the zinc contaminant.

PRE-LAB ASSIGNMENT

1. Explain why X-ray fluorescence is observed when matter absorbs X-rays of sufficient energy. Why does each element have a unique X-ray signature?

2. Convert 6.4 keV X-ray energy to wavelength. 1 eV = 1.602 x 10^{-19} J/eV

EXPERIMENTAL

Get Trained on Safe Use of X-Ray Spectrometer. Our use of X-rays is overseen by the Radiation Safety Committee. To use the spectrometer, you MUST be trained in safe use of x-rays, including a brief overview of x-ray production, hazards and detection. Your TA will go over the safe use of the instrument with you prior to your beginning this experiment. If you arrive late, you cannot work with the instrument until you receive training. You will need to sign a sheet indicating that you have received training in the safe use of the instrument.

Assemble the XRF cells. The cells have plastic bodies and no bottom. You will need to stretch mylar film over the bottom and secure it with the holder. See Figure A1 below to learn how to do this. Be careful – the mylar tears easily, and you don't want the mylar film to become contaminated with Zn!

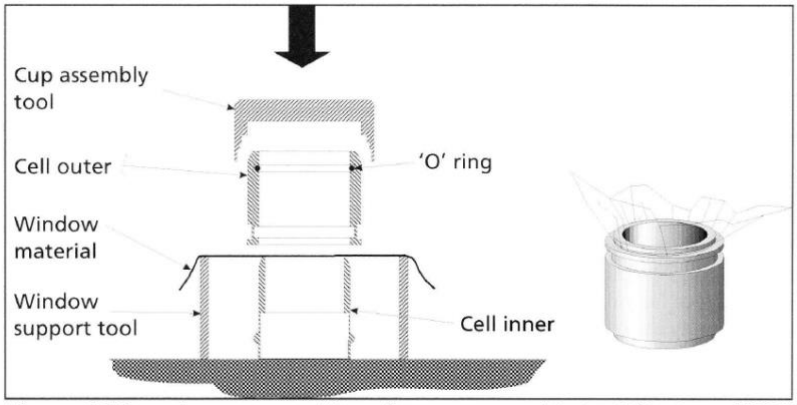

Figure A1 Sample cup assembly using cup assembly tool (Part no. LX1054)
The window assembly tool is also used to dismantle the cell.

Make 6 sample cells from a cell body, piece of mylar film (don't waste it - it is surprisingly expensive stuff!) and the cup tool. Note - you will want to take precautions not to contaminate the films with lab zinc dust from the lab bench or the lab towels at this stage. Your hands likely also are contaminated with zinc, so use clean hands and avoid touching the mylar used for the cell bottoms. Once you have your cells, have the TA check them BEFORE you begin the experiment.

Set up the Experiment in the Software You'll need to set up the experiment in the instrument software. You'll consider several issues:

The *detector* (measurement head): This instrument is not set up with helium purge, so this is simple: you will need to use the PIN detector, NOT the Focus 5+ detector.

The *tube voltage*: This is the energy needed to excite the elemental emission lines. Generally, a tube voltage of about -2x the line energy is needed to excite a particular elemental line. So, if the Fe Ka line occurs at 6.3996 keV, you would select a tube voltage of -13kV as a starting point to measure iron by XRF. What you set here determines which elemental lines you can see; you won't see fluorescent lines above the limit, so this helps with selectivity.

Filters: These are needed to help remove background radiation reaching the sample by removing the low energy radiation of the tube continuum. The PIN detector has a 4-position primary filter: open, A4, A6, and Z1. You'll have to see which one works best for this measurement. The PIN detector has no secondary filter.

Tube current: The tube current setting increases the counts per second (cps) the detector sees. For the PIN detector, there is a limit to the current so that a deadtime limit of 45% is reached. You can see the deadtime value in the 'Spectra' column of the 'Measurement Conditions' table once the spectrum has been acquired. It is best for the analysis and the tube to run below the limiting current.

Measurement Time: This is the time for the acquisition of the spectrum determines the counting statistics, and therefore the precision of a given measurement. Longer counting will not increase signal, but it will reduce the random noise, because noise decreases as the square root of

counting time.

You'll need to use different settings for the qualitative assessment of the wipe sample. Here, you are looking for **what** is there, not **how much** Zn is there. So, you'll want a high tube voltage, and a reasonable but not a long counting time. For the quantitative analysis, you may want a more selective voltage and possibly a longer counting time.

Analysis of the Wipe Sample. You and your partner(s) will work together to analyze a wipe sample collected from a laboratory bench in 241 Brown Laboratory. You will report both qualitative and quantitative analysis of the wipe sample. The quantitative analysis will be for Zn, which should be reported as the mass of Zn present on the wipe in μg.

You will measure the total zinc in the wipe sample by calibration, which may need to be corrected for Zn present in the blank obtained on the mylar films. You will need a measurement of the wipe, the blank, and then at least 3-5 measurements of known volumes of Zn standards spotted on the lab towel.

Be aware that very little zinc is being measured – it is easy to contaminate the sample if you touch it or place on contaminated surfaces!

Qualitative Analysis: The aim here is to get a broad view of what contamination is present in the wipe sample. Try a high tube voltage and do a survey scan. Use the software to identify and label the peaks that you see. Adjust voltage, filters and current to produce a clear spectrum. Label it and print this out.

Quantitative Analysis

Make a standard solution of Zn from the 1000 ppm stock so that ~100 mL of Zn stock adds an appropriate mass of Zn to the towel.

Then, make 6 towel rounds by carefully cutting out circles of lab towel with the scissors. I suggest using towels from the middle of the towels set out, and stacking 3 towels to form the rounds.

Take one of these 3-ply rounds, lightly wet with about 100 μl of distilled water, and wipe the entire surface of a lab bench with it. Take care to try to expose the towel surface evenly, if possible- don't just wipe with a fraction of the towel! Dry the towel in the lab oven for 5 minutes, let cool, then measure its spectrum. Take a second 3-ply towel round and repeat the wipe sample.

Take the other four towel rounds to make a calibration curve by adding aliquots of Zn with the micropipette –aim to span a range above and below the estimated wipe value by 100 mg or so. Dry these aliquot-spotted circles in the lab oven in labeled beakers for 5 minutes. Then, let them cool, load them in the spectrometer, and measure their spectra under the same spectral conditions. Print the spectrum for each, and record the cps (counts per second) for Zn and other experimental settings.

Also measure blanks – a sample cup with just the unexposed towel round and mylar film – under the same conditions as you used for the sample and the calibration curve. You'll need to correct signals for this blank response.

You may need to adjust the concentration of your standard solution, the tube current and counting time depending on signals from the wipe. You may also want to rotate the rounds, so that you get several measurements per round, since it is reasonable to expect that the beam does not sample the full area of the cell.

It is also possible that you'll need more towel rounds for the calibration. Use the same procedure to prepare the samples, adjusting the Zn levels as necessary.

Calibrate the micro-pipette. You will need to know what volume the micropipette delivers at the settings you use. Pre-weigh a weighing bottle and cap to +/- 0.1 mg. Using the micropipette set at 100 μL, add an aliquot of water to the weighing bottle, replace the cap and re-weigh. Repeat 10 times to obtain an average volume delivered and the standard deviation. Repeat the calibration at other volume settings as needed.

Correct for the blank signal on all scans if necessary. Make a calibration plot for the blank-corrected zinc peak height vs. amount of zinc standard added. Calculate the amount of zinc in the wipe sample (in μg) from this plot.

SAFETY AND DISPOSAL

The zinc solutions used in this experiment require only normal handling precautions. Dispose of these in the non-organic waste jug.

Disassemble all XRF cells (follow the method given in Figure A3) and discard the mylar films in the trash. Discard all Zn-containing paper towel samples in the chemical trash.

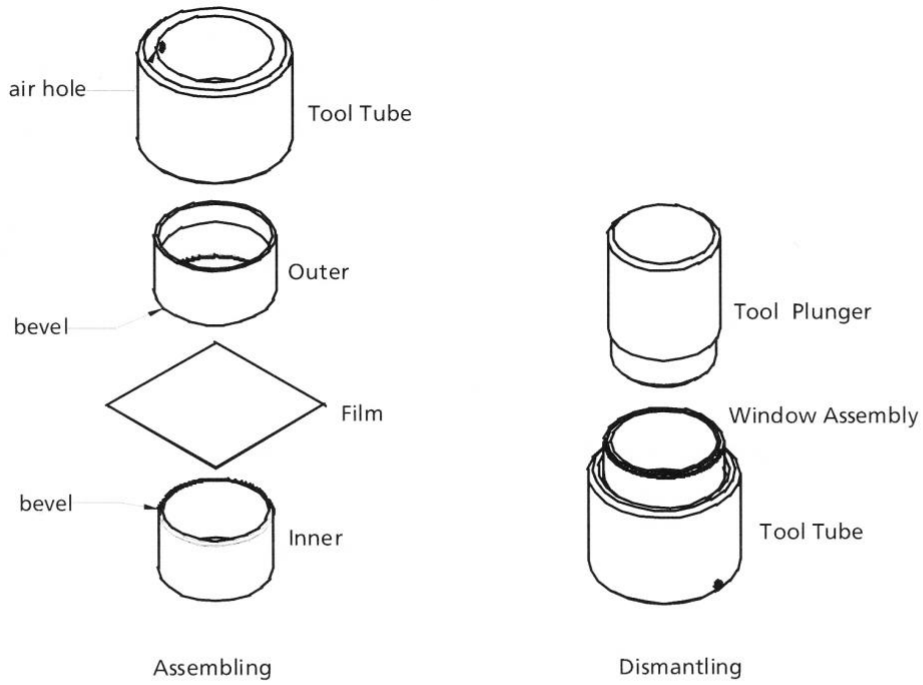

Figure A3 Assembling and Dismantling of secondary safety window (Tool Part no. LX320)

Note: the secondary window clamping ring has a small chamfer on its leading edge and this should face upwards when placed in the recess of the secondary safety window assembly tool.

(From the TwinX Operator Manual)

REPORT

Do a regular report, including an introduction and an error analysis. Report the Zn amount in μg. Include the qualitative scan response with identified peaks and the calibration curve with one XRF scan used for quantitation.

In your discussion, answer the following questions:

1. Explain why Zn is so abundant as a contaminant. Suggest a possible source of the Zn contaminant. What could be done to reduce Zn contamination?

2. XRF is known to be affected by changes in the sample matrix. Why was it necessary to dry all samples in the oven before measuring the XRF spectrum? Explain how the method's sensitivity to the sample matrix can work as a disadvantage for a quantitative contamination analysis done with a wipe sample.

3. You may notice that the Zn has 2 peaks, one larger than the other. Explain why it should be

possible to use both peaks in your analysis, and why the two peaks allow some advantages over a single peak analysis.

4. Often, gloves are suggested in some of the other experiments. Are gloves a good idea for this experiment? What would you need to check to answer this question.