Elemental Analysis by ICP-OES

Introduction:

You are a technician working for a lab which provides analytical chemistry services. Recently a dog boarding situation was discovered in a rural area of your province. Some of the dogs displayed symptoms of poisoning and a large amount of rat poison, containing zinc as the active ingredient, was found in the vicinity of the feeding area. Samples of the feed were given to you to analyze by ICP-OES. Water samples from the dog's dishes as well as the home water supply were also available to analyse. A sample of one of the sick dog's blood was also provided for analysis. You will analyze these samples in an effort to determine whether the dog's poor health was a consequence of poisoning.

Objectives:

The objectives of this experiment are to:

- Develop and apply a method for the ICP-OES sample analysis
- Optimize the instrumental conditions for the analysis
- Use a standard sample prep digestion method to prepare samples

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Questions to be answered before starting the experiment:

1) In a few sentences, describe the theory behind optical (atomic/ionic) emission spectroscopy (OES).
2) How is each element identified in OES? Why it possible to analyse for several elements simultaneously as compared to single analysis as with atomic absorption?
3) What considerations must be taken when selecting a line for an element in analysis of a sample mixture? What is the difference between hard and soft lines?
4) Describe the ideas behind direct comparison and standard addition methods in the analysis of ICP-OES? Draw and explain typical calibration curves you would determine during your analysis.

Materials:

Equipment:

- Varian 725ES ICP-OES with a peristaltic pump, autosampler, computer and software; analytical balance, automatic pipettes (10-1000 µL), disposable pipette tips, various glassware.

A) Sample Digestion and Preparation

Samples were prepared as follows:

1) 2 separate 100 mg samples of the control brand matched dogfood were weighed and placed into "Digiprep" plastic digestion tubes.

2) 2 (100 mg each) scene dogfood sample from the kennel were also weighed.

3) The samples were digested in "digiprep" digestion system located in a fume hood

4) The samples were digested in 3 mls of concentrated nitric acid. The samples were digested for 90 min @ 90^0C. 1 ml of 30% peroxide was added at 45 min to remove carbon in sample.

5) Once cooled; the samples were centrifuged for 10 min @1500 x g to pellet solid material. The supernatant was placed into labelled 50 mL volumetric flasks and brought to volume with **miliQ H_20.**

6) The dog food sample suspected to be high in Zinc were diluted at 1 in 20. The dog blood was diluted to 1 in 10 using 2% $HN0_3$

The tubes containing sample and standards were placed in the autosample rack.

Reagents and Standards:

- Trace element grade, concentrated Nitric Acid, stock standards 1000 mg/L, Milli-Q water, dilution/wash solution: [2% HNO_3 (v/v), 4 L]. The 2% HNO_3 is also your standard blank sample.

- Multi-element calibration standard: A multi-element calibration standard stock solution to be made by students. This is to be made from commercial stock solutions.

- Unknown sample(s) to be determined.

Instrument Optimization and Sample Preparation:

B) Multi Element Stock Preparation:

1) Prepare 50 mls. of a stock solution in a volumetric flask with the following concentration of minerals from the commercial standards (1000ppm) provided. The matrix (diluent) is 2% HNO_3 (v/v).

   Copper and Iron – 50 ppm

   Magnesium - 250 ppm

   Manganese and Zinc – 1 ppm

This is a 10x stock solution from which your standard curve and solution for optimization will be prepared.

2) 50 mls of a 1:5 dilution of the 10x stock solution was prepared to be used for optimization using 2% $HN0_3$

Optimization of Instrument Conditions

It is important to determine optimum operating conditions for each analysis depending upon the element (wavelength/line) of interest. Emission lines free of spectral interference for the element of interest should be chosen. Other important parameters which affect instrument optimization include RF power, viewing height and nebulizer gas flow. An explanation of the theory is available from the HELP menu.

With this instrument; there are two ways to perform optimization. The first is manually; in which the parameters are changed by the operator as a solution is pumped through the instrument. The instrument provides a spectra and the user determines the best settings. The software includes a program (under the tools icon) called "optimax" which performs an automatic optimization based on the range and parameters that you specify. It will increment the settings and then provide optimized values once it has cycled through the range that you specified.

Before performing the optimization a new worksheet must be created and emission lines selected.

Create New Worksheet

1) Open the ***ICP Expert II*** software. Under the file menu by clicking ***New Worksheet*** in the dialog box.
2) Click on the "C" drive, open ICP data/student data/4590/2021. Name the worksheet and include your group number and date in the title.
3) Turn on the argon tank, setting the low pressure gauge to 90 p.s.i. The system will begin its purge. This takes about 20 minutes.

Configure tubing and set up Instrument

4) Secure the pump tubing: Select either pump tubing, and place the bottom and top tab between the bottom and top holders stretching the tubing clockwise over the pump rollers. Repeat for the other tube. **Note that the pump will rotate clockwise, so make sure the tubing is configured in the way so that the tubing will pump the sample into the nebulizer and waste from the spray chamber into to the waste container.**
5) Lock the pressure bars into place by raising the pressure bar onto the tubing and clamp them to their original position. The middle groove of the 3-channel peristaltic pump is reserved for an internal standard or ionization buffer solution and is not used in this experiment.
6) Place the tubing on auto sampler pump and clamp pressure bar.
7) Once the instrument is finished purging turn on the water bath (under counter behind instrument).
8) The temperature of the "Peltier" should drop to -35^{o}C
9) The plasma torch can be lit by clicking on the plasma icon at the top of the screen. ***(this should not be done untill about 10 min before you are ready to make meaurements.)***

Check with an instructor/TA prior to lighting the torch to make sure the configuration is correct. Argon is expensive so use your time well once torch is activated.

Select Lines:

10) Click the *Methods* tab and then the *edit method* button. In the *Method Editor* window under *elements* tab a periodic table is displayed from which lines can be selected.

11) Click on an element in the periodic table to display possible line choices. A wavelength and a graph will appear on the top showing the potential interferences (it is also shown in a table on the right side of the screen). **Choose the wavelength for each element based on:**

    a) Intensity (highest signal to noise ratio on the chart to the left side)

    b) Least interferences (chart on the right side) from elements suspected to be present in your sample

    To select the line(s), simply move the cursor to the line and click on ***OK***. When done click on ***Close*** and update your method. Choose at least two lines for Zn.

Optimizing the Operating Conditions using Automax:

12) Disconnect the sample tubing from the auto sampler at the yellow connector and place the instrument end of tubing into a volumetric containing your 1 in 5 solution of stock standard.

13) In the *Method Editor* window; click the *Conditions* tab. At the top centre of the screen it should state that '**All lines share same conditions'.** If not, go to *Options* tab in the tool bar menu and check it.

14) From the *Tools* menu in the *Method Editor* window select automax.

15) Choose net signal and check the lines you want included in the optimization. The default range of values for the parameters is generally acceptable.

16) Once finished; the instrument will provide the optimized settings and ask if you want to update the method. Choose yes, but make sure you write down the settings as the update function doesn't always work. Before running; verify under the *conditions* tab that the settings are correct.

A) Standard Curve:

1) Prepare a standard curve of 4 serial dilutions of your stock standards solution (each dilution being 1 to 2) using the ICP tubes. You will need a final total volume of 5 mls left in the ICP tube for analysis. The diluent is 2% $HN0_3$

    a. Aliquot 5 mls diluent into tubes # 2-4

    b. Aliquot 10 mls standard into tube #1

    c. Remove 5 mls from tube #1 and add to tube #2 and mix (1 to 2 dilution)

    d. Repeat step c untill tube 4 is reached. (1 to 4)

B) Complete Method:

Input concentrations of the External Standards:

1) In the ***Method Editor*** window click the ***Standards*** tab. All lines chosen will display in a table. Change the number of standards to match what you have.

2) Change the units to ppm and enter the assigned standard concentrations values that you have prepared. #1 should be the least concentrated standard.

3) The lower part of the screen contains curve analysis options. Change the % error to 100% and use the "weighted fit" option. These options can be manipulated after the data acquisition if necessary.

Defining the Sample Sequence

4) Click the ***Sequence*** tab to open *Worksheet samples* table.

5) Click the ***Sequence Editor*** tab on the right side of the screen which will open a new page. Type in the sample count (remember to add one for the blank between the standards and the samples).

6) Check ***Begin with calibration***

7) On the sequence page, click **Auto sampler Setup** tab which will open the Auto sampler Setup page. Make sure the Platen Type is SPS 3, Rack Type is Type 60, use is ***Sample***, and ***Starting tube*** is 1. Close the auto sampler set up page.

8) In the Worksheet Samples table, enter in the sample ID. The first sample should be blank. The calibration blank and the standards will already be shown and are not able to be edited here.

Analysis

9) Place the calibration blank and standards in the first rack. (lowest to highest) and the samples in the second rack according to the sequence sample worksheet.

10) Double check with instructor to verify correct setup.

11) Under the **Analysis** menu click on **the green play button at the top of the screen**. This will start the analysis, beginning with the calibration blank and standards, and then the samples as defined in the sample sequence.

12) Verify the calibration curves for each wavelength. Note that some wavelengths may have failed the calibration for various reasons. There may also be flags associated with your sample values, for example if a sample is out of the range of the standard; it will not be calculated. These can be adjusted; consult TA/instructor if help is required.

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Turning Off the System:

13) Rinse the spray chamber by running the wash solution through the system for about 5 minutes. Run 2% $HN0_3$ water for 5 minutes.\

14) Click the ***Plasma off*** icon. The torch will extinguish and the peristaltic pump will stop.

15) Release the pressure bars and lift the tubes out of the grooves on the pump. Do the same with the pump on the auto sampler.

16) Turn off the water cooler. Wait 5-10 minutes before turning off argon gas.

17) Close the valves to the Argon tank and relieve the pressure regulator. **Leave the main power switch on** to keep the polychromator thermostating system operational.

Data:

The easiest way to collect your data is to copy the values for the standards and samples to "Excel" program and e-mail transfer the results. Your results should determine level of minerals in the dog food samples and the discussion should include whether the levels could cause problems with the dogs consuming the feed, etc.

Questions:

1. The instrument you used was a radial instrument. The ICP-OES can also have an axial torch. What are some disadvantages and/or advantages of an axial versus a radial torch.

2. What is the advantage of using an internal standard in your samples?

3. What other detection system could be attached to an ICP and what advantage would there be?

4. What other procedure could be used and what are advantages or disadvantages.