

LABORATORY EXPERIMENT 11

Determination of microelements (Mn and Cu) in tea leaves

1. MAKING SOLUTIONS FROM THE SAMPLES

With the analytical instruments that most laboratories have, it is necessary to get the elements and other components that we want to determine into solution. The ways of making solutions from the samples are:

- Acid digestions - effectively dissolving the whole sample, or most of it.
- Dry-ashing at 450-550 °C to destroy organic matter, followed by dissolution of the residue in acid.
- Extraction - by hot or cold reagent solutions or solvents

Acid digestion and ashing are usually used to determine the total contents of a component, such as a metal element, being measured. On the other hand, extractions may be targeted at the removal of a fraction of the component. The choice of the actual method used will depend on the purpose of the study. For example, it may be that the total content of a metal element in a plant indicates the requirement for that element to be added as a nutrient. Or, the total content may affect some aspect of further processing or a quality factor such as color, taste or flavor. On the other hand an extraction may be more appropriate to determine the loss of the element in processing or cooking. In this experiment, a hot water extraction is used to measure the quantities of some metals that are released from tea leaves to be consumed in a cup of tea.

In this experiment we will explore the analysis of:

- Total contents - Mn and Cu in tea leaves by ashing and acid digestion
- Extractable contents: hot water extractable Mn and Cu in tea leaves.

It is worth noting that the tea manufacturers have taken care of grinding the tea leaves. Their products are thoroughly homogenized to ensure that the product quality is uniform. Therefore there should be little variation between tea bags of one type of tea.

Mineralization of Tea Samples

The inorganic components (total Mn and Cu) that are to be determined in the tea samples must first be brought into solution. Dry-ashing in a muffle furnace destroys the organic matter in the samples leaving a mineral ash. The ash contains the elements in the form of oxides which dissolve

in acid leaving an insoluble residue of silica.

- Weigh 0.5 g of each sample into a 30 cm³ porcelain crucible and make a note of the exact weight in your notebook .
- Ash the samples in a muffle furnace overnight (16 hours) at 550 °C.
- Allow to cool and add, by pipette, 5 cm³ of 1 M nitric acid (HNO₃) solution.
- In a fume-cupboard, evaporate the samples to dryness on a hotplate at 100 °C.
- Return the samples to the muffle furnace at 550 °C for 15-30 minutes.
- Allow to cool and add 10 cm³ of 1 M nitric acid (HNO₃).
- Filter each sample solution into a 25 mL volumetric flask using Whatman filter papers, No. 2.
- Wash the crucible and filter paper with several portions of 0.1 M HNO₃.
- Make the volume in the flask up to 25 cm³ with 0.1 M HNO₃; stopper and mix well.
- Store the sample solutions for the subsequent determinations of Mn and Cu.

Extraction of Tea Samples

- a) Weigh 3.00 g (± 0.01 g) tea leaves.
- b) Using a measuring cylinder, put 100 cm³ deionized water into a labeled 500 cm³ conical flask.
- c) Place the conical flask on the hotplate and bring the water just to the boil.
- d) Remove the conical flask from the heat and immediately add the weighed sample of tea to it.
- e) Swirl the flask to mix the infusion and allow to stand for 5 minutes ± 15 seconds,
- f) Swirl the infusion thoroughly again and decant a portion (about 30 mL) through the tea strainer and polypropylene funnel, into a 100 cm³ conical flask,
- g) Allow to cool and pipette 10 cm³ of infusion from the 100 mL conical flask into a labeled crucible,
- h) Evaporate the samples in the crucibles to dryness on a hotplate at 100 °C.
- i) Allow to cool, add by pipette 5 mL of 1 M nitric acid (HNO₃) solution, and evaporate to dryness again.
- j) Place the crucibles in the muffle furnace at 550 °C for 15-30 minutes,
- k) Allow to cool and add 10 cm³ of 1 M nitric acid (HNO₃) to dissolve the residue in the crucible.

2. Mn and Cu Determination.

In this experiment, we are going to determine Cu via atomic absorption spectroscopy and Mn via spectrophotometry. In order to make appropriate calibration curves, we need standard solutions of Copper and Manganese.

Mn Standardization by EDTA Titration

Reagents

$MnSO_4 \cdot H_2O$: (1 g/student) This material is **not** a primary standard.

$EDTA$: $Na_2H_2EDTA \cdot 2H_2O$, 1 g/student.

$0.5\ M\ NH_3/NH_4^+$ buffer (pH 10)

Hydroxylamine hydrochloride: ($NH_3OH^+Cl^-$, FM 69.49) 1 g/student.

Eriochrome Black indicator solution

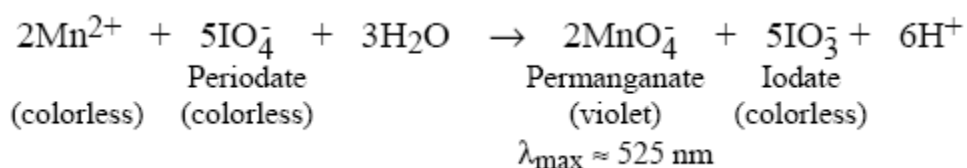
Procedure

- 1. Standard 0.005 M EDTA:** Dry $Na_2H_2EDTA \cdot 2H_2O$ (FM 372.25) at $80^\circ C$ for 1 h and cool in a desiccator. Accurately weigh out $\sim 0.93\ g$ and dissolve it with heating in 400 mL of distilled water in a 500-mL volumetric flask. Cool to room temperature, dilute to the mark, and mix well.
- 2. Mn^{2+} stock solution:** Prepare a solution containing $\sim 1.0\ mg\ Mn/mL$ ($\sim 0.018\ M$) by dissolving $\sim 0.77\ g\ MnSO_4 \cdot H_2O$ (FM 169.01) in a clean plastic screw cap bottle with 250 mL water delivered from a graduated cylinder. Masses and volumes need not be accurate because you will standardize this solution.
- 3.** Rinse a clean 50-mL pipet several times with small volumes of Mn^{2+} stock solution and discard the washings into a chemical waste container. Then pipet 50.00 mL of Mn^{2+} stock solution into a 250-mL volumetric flask. Add $\sim 0.8\ g$ (not accurately weighed) of solid hydroxylamine hydrochloride to the flask, and swirl to dissolve the solid. Add $\sim 40\ mL$ of water and swirl to mix the contents. Dilute to the mark with water, set the cap firmly in place, and invert 20 times to mix the solution. This solution contains $\sim 0.0036\ M\ Mn^{2+}$. The reducing agent, hydroxylamine, maintains manganese in the +2 state.
- 4.** Rinse a 25-mL pipet several times with small volumes of the diluted Mn^{2+} solution from step 3. Pipet 50 mL of the diluted Mn^{2+} solution into a 250-mL Erlenmeyer flask, add 5 mL of pH 10 buffer, and add 1–5 drops of eriochrome black indicator. Titrate with standard EDTA from a 50-mL buret and note the end point when the color changes from red to blue.
- 5.** Repeat step 4 twice more to obtain a total of three replicate titrations. The Erlenmeyer flask must be clean, but it need not be dry for each new titration.
- 6.** From the molarity and volume of standard EDTA required for titration, calculate the molarity and standard deviation of the original $\sim 0.018\ M\ MnSO_4$ stock solution. Express your answer with an appropriate number of significant digits. Calculate concentration of Mn in mg/mL.

Copper solution preparation. Accurately weigh out 0.1000 g of metal copper and dissolve it in 2-3 mL of nitric acid (see experiment 7) in a 100-mL volumetric flask. Cool to room temperature, dilute to the mark, and mix well. This solution contains 1.000 mg/mL Cu.

Spectrophotometric determination of Mn (calibration),

In this experiment, Mn is oxidized to the violet-colored permanganate ion, whose absorbance is measured with a spectrophotometer:



Dilute the sample solution containing no more than 0.2 mg of Mn in a beaker with water to about 15 mL. Add 2.5 mL of conc H₂SO₄, 0.5 mL of conc HNO₃, 0.1 g of KIO₄, and stir. Heat the solution nearly to boiling and keep at about 90° C for 10 min. Cool the solution, transfer it to a 25 mL volumetric flask and dilute to the mark with water. Measure the absorbance of the solution at 528 nm against water.

Atomic Absorption Determination of Copper.

Prepare the instrument as described in operating instructions.

Open the main valves on the compressed air supply line and acetylene tank.

Turn air on, and check the flow rate.

Ignite the burner of the AA spectrophotometer. Set zero absorbance for pure water.

Measure the absorbance of 1.0 ppm standard in triplicate.

Prepare several standards, measure their absorbances, and build the calibration line.

The suggested concentrations are 0.05 ppm, 0.1 ppm, 0.2 ppm, 0.4 ppm, 1.0 ppm, 2.0 ppm.

Analyze the solutions resulted from the tea leaves digestion and calculate the amount of Cu in tea leaves in ppm (µg/g).

Manganese determination. From the 25 mL flask, take 10 mL of solution, add 2 mL of conc, H₂SO₄, 0.5 mL of conc. HNO₃, 0.1 g of KIO₄ and stir. Heat the solution nearly to boiling and keep at about 90° C for 10 min. Cool the solution, transfer it to a 25 mL volumetric flask and dilute to the mark with water. Measure the absorbance of the solution at 528 nm against water. Calculate the amount of Mn in leaves in ppm (µg/g).