A foggy morning on a metal recycling plant

Focus group: Upper secondary school students. The experiment has been developed for the Finnish national curriculum course KE4, where students learn about materials used in industry and reduction-oxidation reactions. It can also be used with students in upper comprehensive school if the theory and calculations are simplified.

Length: About 60 min

Motivation: In this experiment the students are employees at a metal recycling plant. A customer brings a large amount of metallic material to the recycling plant and asks how much it is worth. The students should figure out the price of the metallic material, knowing that the recycling plant pays 2 €/kg for copper.

Aim: The aim of the experiment is to teach the students about sample preparation and what it is like to work in a laboratory. Students will be familiarised with the principle and usage of a spectrophotometer, and how calibration graphs are drawn.

Key words: Concentration – Spectrophotometry – Absorbance – Conversion figure – Recycling – Metals

SAFETY AND WASTE DISPOSAL

- Wear a laboratory coat, safety goggles and gloves during the experiment. Splatters on the skin and in the eyes should be washed **immediately** with plenty of water. Seek medical help if necessary.
- Concentrated nitric acid is a strong and very corrosive acid. It must be handled only by teachers.
- Ammonia is a strong base. It can corrode and dry skin.
- Dissolving copper in concentrated nitric acid releases toxic nitrogen dioxide. Do the dissolving in a **fume hood**.

- Copper solutions are inorganic waste and should be collected in waste-bottles for inorganic waste containing heavy metals.

STORY

You work at a metal recycling plant. A customer brings in 1200 kg of yellowish metallic material, that they have found in their storehouse. The customer knows that the recycling plant pays 2 €/kg for copper and wants to know the value of the metal they brought. According to the customer, the metallic material consists of at least 50 % of copper.

What will you do?

a) Ask if the client would accept an offer of 1000 €.
b) Analyse how much copper the metallic material contains and pay the client based on your result.

INTRODUCING QUESTIONS

Although copper is a noble metal it reacts with nitric acid. Why? Write the reaction between metallic copper and concentrated nitric acid, and the reaction between metallic copper and dilute nitric acid. How do the reactions differ?

Concentrated nitric acid oxidizes copper to the oxidation state +II, while the oxidation state of nitrogen changes from +V to +IV. Brown NO_2 is formed in the reaction.

$Cu + 4\ HNO_3 \rightarrow Cu(NO_3)_2 + 2\ NO_2 + 2\ H_2O$

If dilute nitric acid is used the oxidation state of nitrogen is reduced to +II and colourless nitrogen monoxide is formed.

$3\ Cu + 8\ HNO_3 \rightarrow 3\ Cu(NO_3)_2 + 2\ NO + 4\ H_2O$

Copper is used as pure metal and in metal mixtures, also known as alloys. What kind of copper alloys are there and what are they used for?

The table below contains a list of copper-alloys.

Alloy	**Main components of the alloy**
Brass	Copper and zinc
Bronz	Copper and tin
Constantan	Copper and nickel
Nickel silver	Copper, nickel and zinc

Why is copper recycled and why does the recycling plant pay customers for the copper they bring in for recycling?

Recycled copper can be used in the production of new copper-containing products. Industries buy recycled copper if it is pure enough and priced well. By paying customers the recycling plant wants to motivate people to recycle their copper.

BACKGROUND

Concentrated nitric acid oxidizes metallic copper.

$Cu + 4\ HNO_3 \rightarrow Cu(NO_3)_2 + 2\ NO_2 + 2\ H_2O$

Copper-ions with ammonia form a blue compound called tetraamminecopper(II) ion.

$Cu^{2+} + 4\ NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$

To determine the copper concentration of the metallic material, it must be dissolved. The metal is dissolved in nitric acid and the solution is mixed with ammonia solution. The copper ions form tetraamminecopper(II) ions that give the solution a blue colour. The more tetraamminecopper(II) ions there are, the stronger the blue colour in the solution is. The intensity of the blue colour can be measured with a spectrophotometer. The concentration of a sample solution is determined by comparing its intensity with the intensities of solutions of known copper concentrations.

REAGENTS

- Metallic material, e.g. brass nails
- Concentrated nitric acid
- 5 % ammonia solution
- Distilled or ion exchanged water
- Standard copper solutions (prepared by the teacher in advance)

EQUIPMENT

- Glass test tube
- Funnel
- 50 ml volumetric flask
- Measuring cylinder
- Cuvettes and spectrophotometer
- Pipettes
- Scale

INSTRUCTIONS

PREPARATION OF SOLUTIONS (TEACHER)

5 % ammonia: Dilute 100 ml of 25 % ammonia with distilled or ion exchanged water to 500 ml in a volumetric flask.

First copper solution (4 g/l): Dissolve 3,143 g of $CuSO_4 \cdot 5\ H_2O$ in 200 ml of distilled or ion exchanged water. Prepare the solution in a volumetric flask.

Standard solution, 200 mg/l: Measure 25 ml of the 5 % ammonia solution in a 100 ml volumetric flask. Add 2 ml of concentrated nitric acid and 5 ml of the first copper solution (4 g Cu / l) and fill the flask to its graduation mark with distilled or ion exchanged water.

Standard solution, 1000 mg/l: Measure 25 ml of the 5 % ammonia solution in a 100 ml volumetric flask. Add 2 ml of concentrated nitric acid and 25 ml of the first copper solution (4 g Cu / l) and fill the flask to its graduation mark with distilled or ion exchanged water.

SAMPLE PREPARATION

Weigh about 0.05 g of the metallic material and remember to write the exact weight of your sample in the results table (next page). In a fume hood, put the metallic material into a test tube in which the teacher has put 1 ml of concentrated nitric acid.

When the sample has dissolved pour the solution in a 50 ml volumetric flask. Add 13 ml of 5 % ammonia in the flask. Fill the test tube with distilled or ion exchanged water and pour the contents of the test tube in the volumetric flask. Fill the flask to its graduation mark with distilled or ion exchanged water (use a pipette for precision) and mix until the solution is homogenized.

MEASUREMENTS

Fill a cuvette with your solution using a pipette and measure its absorbance at the wavelength 600 nm. Write down the absorbance in the results table. Note that you should not touch the clear sides of the cuvette, since fingerprints will defect the measurement. Repeat the measurement for the standard solutions prepared by the teacher. Write the results of your measurements in the table below.

RESULTS

	A	c (mg/l)	m(g)
Dilute standard solution		200	-
Concentrated standard solution		1000	-
Metal sample			

The relation between the absorbance and concentration of a solution is given by Beer-Lambert's law:

$A = \varepsilon \cdot b \cdot c$,

where A is the absorbance, ε is the absorptivity of the solution (constant), b is the optical path length (constant), and c is the concentration of the solution. As we can see from the formula, the absorbance of a solution is proportional to its concentration.

Draw a calibration graph using the measured absorbances of the standard solutions. You can draw the calibration figure on paper or use a computer programme. Determine the copper concentration of the sample solution using its absorbance and the calibration graph. Calculate how much copper there was in the metallic material the customer brought and how much it is worth. You can let a computer program do the calculations for you.

CONCLUDING QUESTION

How many kilograms of copper does the 1200 kilograms of metallic material contain, assuming the copper concentration is the same throughout the material? How much should the customer be paid based on the copper content of the material?

Read from the calibration graph the concentration based on the absorbance you measured for the sample solution and calculate the total copper mass and the price of the metal using the equations below.

Total copper mass (in kg) = (Volume of sample solution · Concentration of sample-solution · 1200 kg)/Mass of sample = (0,05 [l] · c [mg/l] · 1200 kg) / m [mg]

Payment = Amount · 2 €/kg

The exact copper concentration and payment can also be calculated using excel.

The values of metals keep changing, which also affects the payments metal recycling plants can give to their customers. When the prices of metals are high the recycling plants can afford better payments for materials brought in for recycling, and when the prices are low the payments are smaller. This can affect the amount of metal that brought in for recycling. Do you think the payments for metallic materials brought for recycling should be high regardless of the value of metals? Explain your reasoning.

A low price for metals might decrease the amount of metallic material that is recycled. Then industries must buy their metal or metal ores from producers abroad and the *foreign trade capacity (= value of export - value of import) is weakened. From this point of view, it would be beneficial for the society if the payments for metallic material brought in for recycling would be high regardless of the current values of metals.*

The problem can also be discussed from the perspective of energy usage. Less energy is needed to purify recycled metals than producing them from metal ores.