

Grand Prix Chimique
Zagreb, Croatia
25th-30th August 2007

ANALYTICAL TASK

EXPERIMENTAL PROCEDURE

**Complexometric determination of zinc after separation
from cadmium by ion chromatography**

It is almost impossible to correctly determine the content of zinc(II) ions in aqueous solution using complexometric titration if cadmium(II) ions are present. To overcome this problem, zinc(II) and cadmium(II) ions are usually separated before the titration using ion chromatography. Following the chromatographic separation, concentrations of zinc(II) and cadmium(II) ions in the eluents are determined separately. The stationary phase for the separation is an ion exchanger resin in the chloride form, to which zinc(II) and cadmium(II) ions bind as anionic chloro-complexes. Zinc(II) ions are eluted from the ion exchanger resin using a sodium hydroxide solution ($c = 2 \text{ mol L}^{-1}$) that contains 20 g sodium chloride per liter, while cadmium(II) ions are left bonded to the ionic exchanger. Afterwards, cadmium (II) ions are eluted using an aqueous solution of nitric acid ($c = 2 \text{ mol L}^{-1}$).

List of the glassware and laboratory tools on the desk

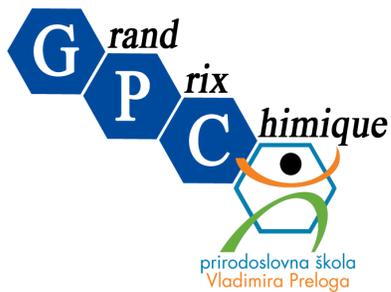
| Item | Number | Item | Number |
|---------------------------|--------|--------------------------|--------|
| Column | 1 | Volumetric flask 500 mL | 1 |
| Erlenmeyer flask 250 mL | 2 | Volumetric flask 100 mL | 1 |
| Erlenmeyer flask 500 mL | 2 | Volumetric pipette 25 mL | 1 |
| Beaker 100 mL | 2 | Glass rod | 2 |
| Beaker 250 mL | 2 | Dropper | 2 |
| Graduated cylinder 100 mL | 1 | Three-way safety bulb | 1 |
| Graduated cylinder 10 mL | 1 | Bottle for Reagent II | 1 |

There is one automatic burette on every side of the desk, shared between two competitors.

Bottles of concentrated hydrochloric acid are located in the fumehoods.

List of chemicals

| | |
|--|--|
| Reagent I | bench |
| Reagent II | bench |
| HNO_3 , $c = 2 \text{ mol L}^{-1}$ | bench |
| $\text{NH}_3(\text{aq}) / \text{NH}_4\text{Cl}$ buffer, pH = 10 | desk , shared by two competitors |
| NaOH , $w = 20 \%$ | desk , shared by two competitors |
| Eriochrome Black T (EBT) | desk , shared by two competitors |
| EDTA disodium solution, $c = 0.0500 \text{ mol L}^{-1}$ (EthyleneDiamineTetraceticAcid) | desk , shared by two competitors |
| Sodium chloride | desk , shared by two competitors |
| Ion exchanger resin | weighing desk , shared by all competitors |



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| Reagent | R codes | S codes |
|---|--------------------------------------|-------------------|
| NaCl(s); analytical grade | | |
| CdSO ₄ (s); analytical grade | 45/46/60-61-25-26-48-23- 25-50-53 | 53-45-60-61 |
| ZnSO ₄ · 7 H ₂ O(s); analytical grade | 22-41-50-53 | 22-26-39-46-60-61 |
| Hydrochloric acid, concentrated | 34-37 | 26-36-37-39-45 |
| Hydrochloric acid, $c = 0,1 \text{ mol L}^{-1}$ | - | - |
| Nitric acid, $c = 2 \text{ mol L}^{-1}$ | 35 | 23-26-36-45 |
| Sodium hydroxide(s); p.a. | 35 | 26-37-39-45 |
| Sodium hydroxide, $c = 2 \text{ mol L}^{-1}$ | - | - |
| Sodium hydroxide, $w = 20 \%$ | - | - |
| EDTA disodium solution, $c = 0.0500 \text{ mol L}^{-1}$ | 36-38 | 26-36 |
| Ammonia buffer solution, pH = 10 | - | 23-24-25 |
| Eriochrome Black T | - | - |
| Distilled water | | |

PART I - Column preparation

Attach the chromatographic column to a laboratory stand, make sure it is securely fastened in the vertical position, and tighten the clamp. Weigh 10 g of dry ion exchanger and place it in distilled water to swell for approximately 1 hour. To pack the column, apply the mixture of the swollen exchanger and water to the column and allow water to drain slowly from the column. While the exchanger is settling, tap the column gently with a glass rod to achieve tight packing of the exchanger in the column. Drain the liquid from the column until the level of the liquid phase is 1-3 cm above the surface of the exchanger. Make sure there are no air bubbles in the packed column.

It is important not to let the prepared ion exchange column to dry!

Apply 80 mL of Reagent I to the column and elute it from the column. The column is now ready for the separation.

PART II - Preparation of Reagent II

Reagent I – already prepared (100 g of NaCl dissolved in 1 L of 0.1 mol L⁻¹ HCl)
Reagent II – weigh 10 g of NaCl and dissolve in a 2 mol L⁻¹ NaOH solution using a 0.5 L volumetric flask

PART III - Adsorption of zinc(II) and cadmium(II) chlorocomplexes on the ion exchanger

Fill the volumetric flask which contains sample for the analysis with Reagent I. Apply an aliquot of 25.00 mL of the obtained solution to the column. Add the sample quantitatively to the top of the column. Adjust the solvent flow to obtain a flow rate of approximately 4 mL min⁻¹.

PART IV - Elution of Zn and Cd chlorocomplexes

Reagent II is the solution for eluting zinc(II) ions. Add 60 mL of Reagent II slowly to the column and elute the column with the same flow rate as previously. The obtained fraction contains zinc(II) ions and should be collected into the appropriate Erlenmeyer flask.

After elution of zinc(II) ions, add 50 mL of distilled water and pass it through the column.

Elute cadmium(II) ions from the column using 100 mL of 2 mol L⁻¹ HNO₃ solution. This fraction should be collected in the 500 mL Erlenmeyer flask.

PART V - Determination of the content of zinc(II) ions

The fraction that contains zinc(II) ions must be neutralized by the addition of concentrated HCl. Add 5 mL concentrated HCl to the fraction and then continue to add the acid dropwise, slowly and carefully, until a precipitate forms (in the case of smaller amounts of zinc(II), there is no visible precipitate and the pH value of the solution should be monitored all the time during the HCl addition). After completing the neutralization procedure, add 5 mL of buffer solution (pH = 10) and approximately 100 mg of the Eriochrome Black T indicator. Titrate the prepared solution with a standardized EDTA solution ($c = 0.0500 \text{ mol L}^{-1}$) until the indicator changes color from wine-reddish to blue.

PART VI . Handling the fraction containing cadmium(II) ions

The fraction containing cadmium(II) ions must be neutralized with a solution of NaOH ($w = 0.20$). Add 30 mL of NaOH ($w = 0.20$) to the fraction and then continue to add it dropwise, slowly and carefully, until the solution is neutralized. A universal indicator paper is provided to monitor the pH of the solution during NaOH addition.

PART VII - Repeated analytical procedure

To ensure the necessary analytical precision of the procedure, the separation and the complexometric titration must be repeated. The column must be regenerated before the separation of the second aliquot of the sample. Add 80 mL of Reagent I to the column and elute it from the column. The column is now prepared for the next separation step.

PART VIII - Calculating the concentration of zinc(II) ions

The concentration of zinc(II) ions in the sample should be calculated by using the experimental results obtained from two titrations.

Result should be presented as a $\gamma(\text{Zn}) / \text{mg L}^{-1}$.

$[A_r(\text{Zn}) = 65.39]$

Chemical reactions

