GRAND PRIX CHIMIQUE

PETNICA SCIENCE CENTER, VALJEVO, SERBIA

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ANALYTICAL TASK

Permanganometric determination of calcium after precipitation as calcium oxalate

Spectrophotometric determination of the pH value of an unknown sample

SUPPORTED BY

Serbian Chemical Society

Ministry of Science, Education and Technological Development of the Republic of Serbia

Faculty of Chemistry, University of Belgrade

Innovation Center of the Faculty of Chemistry, University of Belgrade

Faculty of Science, University of Kragujevac

Available equipment and chemicals

A list of glassware and laboratory equipment on each workbench

Item	Qty	Item	Qty
Beaker, 100 mL	4	Pasteur pipette, glass	2
Beaker, 150 mL	1	Pasteur pipette, plastic	5
Beaker, 250 mL	4	Pipette filler	1
Burette clamp	1	Ring stand	1
Burette, 25 mL	1	Rubber bulb	1
Cloth	1	Scissors	1
Dark surface	1	Spatula, plastic	2
Erlenmeyer flask, 250 mL	3	Tweezers	1
Filter paper	1	Volumetric flask, 100 mL	2
Funnel	2	Volumetric flask, 500 mL	1
Glass rod	1	Volumetric pipette, 20 mL	1
Graduated cylinder, 10 mL	2	Volumetric pipette, 25 mL	1
Graduated cylinder, 25 mL	1	Wash bottle (distilled water)	1
Magnetic stirrer	1	Watch glass	4

Technical balances and ultrasonic baths are available on the weighing desk. Analytical balances and spectrophotometers are located in a separate room.

A list of available chemicals and their locations

Chemical	Location	Chemical	Location
Ammonium oxalate, solid	weighing desk	Ammonium oxalate, 0.25 M	each workbench
Methyl red	fume hood	HCl, concentrated	fume hood
Ammonia, 1:1 solution	each workbench	NaOH, pellets	weighing desk
$Ca(NO_3)_2$	each workbench	Bromocresol green	separate room
$KMnO_4$, standard solution	shared by two workbenches	Distilled water (in wash bottle)	each workbench

Safety considerations

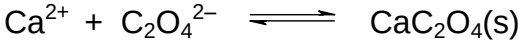
A pair of protective goggles is provided on each workbench. Protective gloves can be found at the weighing desk.

A list of risk (R) and safety (S) statements for chemicals which will be handled

Chemical	R statements	S statements
Ammonia, 1:1 solution	22-34-50	26-36/37/39-45-61
Ammonium oxalate	21/22	36/37
Bromocresol green	11-20/21/22-36/37/38-67	7-16-24/25-26-36-37/39
$Ca(NO_3)_2$	8-22-36/37/38-41	17-26-36/37/39
Distilled water	–	–
HCl, concentrated	2-10-11-12-19-20/22-34-35-36/37/38-39/23/24/25-40-41-66-67	9-16-26-29-33-36/37/39-45-46
$KMnO_4$, standard solution	8-22-34-36/38-50/53-51/53-52/53	26-36-60-61
Methyl red	10-11-34-36/37/38-39/23/24/25-51/53-68/20/21/22	7-16-22-24/25-26-33-36/37/39-45-61
NaOH, pellets	34-35-36/38	24/25-26-36/37/39-45

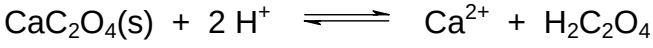
Problem 1: Permanganometric determination of calcium after precipitation as calcium oxalate

A classical and widely applied method for determination of calcium, suitable for biological material, is permanganometric titration method. The goal of this task is to determine calcium previously precipitated as calcium oxalate and quantitatively separated from solution by filtration:



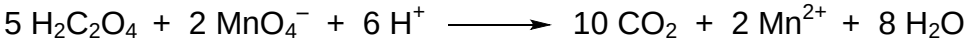
$$Ca^{2+} + C_2O_4^{2-} \rightleftharpoons CaC_2O_4(s)$$

The precipitate is subsequently dissolved in sulfuric acid:



$$CaC_2O_4(s) + 2\,H^+ \rightleftharpoons Ca^{2+} + H_2C_2O_4$$

The liberated oxalic acid is titrated with a standard solution of potassium permanganate:



$$5\,H_2C_2O_4 + 2\,MnO_4^- + 6\,H^+ \longrightarrow 10\,CO_2 + 2\,Mn^{2+} + 8\,H_2O$$

This method is convenient for selective determination of calcium in the presence of magnesium.

Procedure

1. Fill the 100-mL volumetric flask containing the sample to the mark.

2. Prepare 100 mL of sulfuric acid with a concentration of ca. 3 mol/L starting from concentrated sulfuric acid (96%, density 1.84 g/mL). *Be cautious when working with sulfuric acid!*

Calculation:

_____ mL of cc H_2SO_4 to be diluted to 100 mL

Note: Show the calculations for preparing this solution to the jury members, before continuation of your work! If you are unable to calculate the required amount of concentrated sulfuric acid, a jury member will give you the necessary data.

3. Measure out two 25.00-mL aliquots of the diluted solution of the sample into 250-mL beakers using a pipette. To each of them add 10 mL of 3 mol/L sulfuric acid solution and 50 mL of water.

Hot solutions of acid are to be handled in the following steps. Take care while doing so!

4. Cover each beaker with a watch glass and carefully heat their contents on a hotplate until the solutions become hot, but not hot enough to start boiling.

5. Remove the beakers from the hotplate and carefully add solid ammonium oxalate (1.5 g) to each of them. Stir their contents until most of the ammonium oxalate has dissolved.

6. Add 5-10 drops of the methyl red indicator to each beaker, and while the solutions are still hot, increase their pH values by adding ammonia (1:1) while constantly stirring until the first color change from pink to orange. If a greater quantity of ammonia is added, the color of the solution becomes yellow. If this were to happen, add a drop of the previously prepared 3 mol/L sulfuric acid to lower the pH, and then repeat the pH adjustment with ammonia.

7. Leave the solution to stand for at least one hour for the calcium oxalate to precipitate quantitatively. Do not stir the solution during this period.

8. Filter off a majority of the solution into a 250-mL Erlenmeyer flask. Rinse the watch glass as well.

9. Determine whether the filtrate contains traces of calcium ions by transferring a drop of it onto a dark surface and adding a drop of 0.25 mol/L ammonium oxalate solution. If it becomes turbid or a precipitate forms, this means that the precipitation of calcium oxalate did not proceed quantitatively. Potential causes include inadequately adjusted solution pH or insufficient precipitation time. In this case, these parameters should be adjusted more carefully in the next aliquot trial. You should decide whether to continue working with the first aliquot.

10. If there are no calcium ions left in the filtrate, quantitatively transfer all of the precipitate onto the funnel.

11. Rinse the precipitate four times with 10 mL of water. Discard the filtrates.

12. Rinse the precipitate one more time with 10 mL of water. Test this filtrate for traces of oxalate by adding a saturated solution of calcium nitrate to a drop of the filtrate placed on a dark surface. If it becomes turbid or a white precipitate forms, carry on rinsing and testing the filtrate until you obtain one that does not contain any oxalate.

13. When the precipitate is free of oxalate, discard the filtrates.

14. Transfer the filter paper with the precipitate into a 250-mL beaker, and add 25 mL of 3 mol/L sulfuric acid solution and expose to ultrasound until complete dissolution. Decant the resulting solution into an Erlenmeyer flask, and rinse the filter paper with 25 mL water also by exposing the contents of the beaker to ultrasound. Rinse the filter paper once more with 25 mL of water, without the aid of the ultrasonic bath.

15. Heat the solution in the Erlenmeyer flask at temperature above 60 ^{o}C (white fumes must be present above the solution), and titrate the solution using a standard solution of potassium permanganate, while maintaining the temperature above 60 ^{o}C during the titration.

Consumed volumes of the titrant are:

V_1 = _____ mL

V_2 = _____ mL

V_3 = _____ mL

Determine the mass of calcium in the 100-mL sample.

Calculation:

m = _____ g

The relative atomic mass of calcium is 40.08.

The concentration of the standard solution of $KMnO_4$ is 0.0206 mol/L.

Problem 2: Spectrophotometric determination of the pH value of an unknown sample

Typical procedure for measuring pH values is based on potentiometry. However, with some samples, e.g. seawater, confounding complications to the potentiometric measurement may occur, so that spectrophotometric analysis using pH-sensitive indicator dyes can be a good choice for pH measurement.

The pH value of an unknown sample can be determined by adding an acid/base indicator of known K_a and spectrophotometric measurement of relative concentrations of the acid and base indicator forms.

The relationship between the two indicator forms in aqueous solutions is described by the equilibrium:

$$HIn + H_2O \rightleftharpoons H_3O^+ + In^-$$

where

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]}$$

and

$$pH = pK_a + \log\frac{[In^-]}{[HIn]} = pK_a + \log\frac{c_b}{c_a}$$

where c_b and c_a stand for concentrations of basic and acidic forms, respectively.

Once the ratio $[In^-]/[HIn]$ is measured, the pH value of an unknown solution can be calculated using a known value of K_a.

In this problem you will be using bromocresol green, for which the K_a value is 1.6×10^{-5}.

1. In order to determine the concentration of the acid and base forms of the indicator in a mixture it is necessary to first determine the molar extinction coefficient of each form separately.

2. In preliminary experiments absorption spectra of the acid and base indicator forms will be recorded separately, in the wavelength range of 400-650 nm. Those spectra will enable you to choose the most convenient wavelengths for the determination of the extinction coefficients (ε) of the acid and base indicator forms according to the Beer-Lambert law, $A = \varepsilon bc$. For the two selected wavelengths, it is possible to determine the molar extinction coefficients for the acid (ε_{1a} and ε_{2a}) and base indicator form (ε_{1b} and ε_{2b}). Subscripts 1 and 2 denote the first and second chosen wavelength respectively, while subscripts a and b denote the acid and base indicator form respectively.

3. Absorbance of an unknown solution at chosen wavelengths is equal to the sum of absorbances of each indicator form present in the mixture.

$$A_{\lambda 1} = \varepsilon_{1a}\, b\, c_a + \varepsilon_{1b}\, b\, c_b \qquad (1)$$

$$A_{\lambda 2} = \varepsilon_{2a}\, b\, c_a + \varepsilon_{2b}\, b\, c_b \qquad (2)$$

You can calculate the concentration ratio of the base and acid indicator forms using equations (1) and (2).

Procedure

The molar mass of bromocresol green is 698 g/mol.

1. Weigh out 40.0 mg of bromocresol green (with an accuracy of ±0.1 mg).

2. Dissolve the measured quantity of the indicator in water in a 500-mL volumetric flask by filling it to the mark.

3. Prepare a ca. 0.5 M solution of HCl by diluting 3 mL of concentrated HCl with water to the total volume of 75 mL.

4. Prepare a ca. 0.4 M solution of NaOH by dissolving 1.2 g of NaOH in water to the total volume of 75 mL.

Preparation of the solution needed to record the spectrum of the acid indicator form

5. Take an aliquot of 20.00 mL from the prepared solution of bromocresol green and transfer it into a 100-mL volumetric flask. Add 25 mL of 0.5 M HCl to the flask, fill to the mark, and mix well.

Preparation of the solution needed to record the spectrum of the base indicator form

6. Take an aliquot of 20.00 mL from the prepared solution of bromocresol green and transfer it into a 100-mL volumetric flask. Add 25 mL of 0.4 M NaOH, fill to the mark, and mix well.

7. Record the absorption spectra of separate acid and base indicator forms in the wavelength range of 400-650 nm using distilled water as a blank.

8. Choose two wavelengths from the obtained spectra that would be most convenient for the determination of molar extinction coefficients of the acid (ε_{1a} and ε_{2a}) and base indicator forms (ε_{1b} and ε_{2b}). Measure absorbances for both solutions at both selected wavelengths, and calculate the respective molar extinction coefficients.

b = 1 cm

Chosen wavelengths:

λ_1 = _____ nm λ_2 = _____ nm

M(bromocresol green) = 698 g/mol

$c_{indicator}$ = _____ mol/dm^3

Calculation of molar extinction coefficients of the acid indicator form (ε_{1a} and ε_{2a}):

A_{1a} = _____ A_{2a} = _____

ε_{1a} = _____ M^{-1} cm^{-1} ε_{2a} = _____ M^{-1} cm^{-1}

Calculation of molar extinction coefficients of the base indicator form (ε_{1b} and ε_{2b}):

A_{1b} = _____ A_{2b} = _____

ε_{1b} = _____ M^{-1} cm^{-1} ε_{2b} = _____ M^{-1} cm^{-1}

Determination of the pH value of an unknown sample

9. Take an aliquot of 20.00 mL from the prepared solution of bromocresol green and transfer it into a 100-mL volumetric flask containing 50.0 mL of a buffer solution with an unknown pH value, fill to the mark, and mix well.

10. Record the absorbances of the solution at the previously chosen wavelengths. Calculate the concentration ratio of the base and acid indicator forms, using equations (1) and (2), and then calculate pH.

Calculation of the c_b/c_a ratio:

A_1 = _____ A_2 = _____

c_b/c_a = _____

Calculation of the pH value of the unknown sample:

pH = _____