The 49th INTERNATIONAL MENDELEEV CHEMISTRY OLYMPIAD

May 3-10, 2015

Erevan

PRACTICAL EXAMINATION

Erevan

2015

GENERAL REMARKS

1. Throughout the whole exam wear lab coat and protection (or your own) glasses.

2. Take precautions when handling solutions of acids, alkali, and oxidizers!

3. Fill pipettes using pipette filler only. It is absolutely prohibited to suck solutions into the pipette.

4. Take into account that the amount of the provided solutions is limited. A spilled or completely used up solution will be replaced with penalty.

5. You are provided with clean dry pipettes. Do not spend the solutions for rinsing pipettes.

6. When working do not interfere with other Olympiad participants. Keep your working place in order.

7. Pour used solutions into nearest sink (larger or smaller).

8. Use the back side of the booklet sheets for your draft work.

Equipment and glassware (per each participant)

Laboratory stand with a clamp for burette	1
10 mL graduated pipette (for the sample)	1
100 mL volumetric flask (for the sample)	1
100 mL conical flask for titration	1
250 mL conical flask for titration	1
Watch glass	2
10 mL graduated test tube (**to be used instead of the measuring cylinder**)	2
Burette	1
25-50 mL glass beaker	1
Rubber bulb	1
Funnel (for filling the burette)	1
Rack for test tubes	1
Test tubes (to carry out disclosure reactions)	10
Glass vial (empty, with a stopper)	1
Eppendorf tube (empty)	3
Wash bottle with distilled water	1
Spatula	1
Glass rod	1
Eyedropper (in a case):	totally 8
For pipetting reagent solutions	4
Fort carrying out detection reactions	4
Paper towels (couch roll)	1 per table

Reagents

Quantitative analysis (per each participant):

Formaldehyde, 20% solution (in a 60 mL container)

NaOH, 0.09570 M solution (in a 60 mL container)

$NaHCO_3$, 8% solution (in a 50 mL bottle)

KBr, 8% solution (in a 50 mL bottle)

KI, 16% solution (in a 50 mL bottle)

H_2SO_4, solution 1:6 (vol.) (in a 100 mL bottle)

$Na_2S_2O_3$, 0.1000 M solution (in a 100 mL bottle, the bottle for refilling is placed under the fume hood).

On the table for 3 participants:

Starch, 0.5% solution (in a glass vial, pipette with an eyedropper; keep eyedroppers in vials so that eyedroppers are not mixed up).

HCl, ~ 0.1 M solution (in a glass vial, pipette with an eyedropper)

Methyl orange, 0.1% solution (in a glass vial, pipette with an eyedropper)

Phenolphthalein, 1% solution (in a glass vial, pipette with an eyedropper)

Under the fume hood (one set per laboratory)

NaOCl, ~0.18 M solution (in plastic bottles; to refill from the burette under the fume hood)

$Na_2S_2O_3$, 0.1000 M solution for refilling into students' bottles

H_2SO_4, solution 1:6 (vol.) for refilling into students' bottles

Qualitative analysis (per each participant)

Sulfuric acid, 1:2 (vol.) (in a glass vial, pipette with an eyedropper)

Silver nitrate, 0.1M (in a glass vial, pipette with an eyedropper)

NaOH, 0.1M (in a glass vial, pipette with an eyedropper)

Barium nitrate, 0.1M (in a glass vial, pipette with an eyedropper)

pH test paper (in a Petri dish)

Samples

Quantitative analysis

Solution of a sample of a mixed fertilizer, in an volumetric flask

Qualitative analysis

Samples of straight (individual) fertilizers, in Eppendorf tubes (labeled 1 to 9).

Mineral fertilizers are inorganic compounds containing elements (mostly potassium, phosphorus, and nitrogen) vitally important for plants. A fertilizer bioaccessibility depends on the chemical form which the above elements are present in. Qualitative and/or qualitative analysis is needed when a fertilizer lacks the product documentation or has been subjected to a long-term storage. In this work you will carry out qualitative determination of unknown samples of straight mineral fertilizers as well as quantitative determination of a solution of a mixed fertilizer composition.

Part 1. Quantitative analysis

You will find a solution of a real mixed fertilizer composed of carbamide (urea) and ammonium nitrate is placed in the volumetric flask You are expected to carry out quantitative analysis of the fertilizer solution and determine the fractions of nitrogen present in the forms of nitrate, ammonium and carbamide. Carefully fill in to the mark with distilled water and mix the prepared solution well (apply the flask stopper and turn the flask top to bottom for at least 10 times).

Read the procedure with due attention and do your time planning before you start the experimental work. Strictly follow the procedure and wash well the titration flasks between the titrations.

Titration # 1. Determination of the ammonium nitrogen content

The interaction between ammonium ion and formaldehyde affording an acid and urothropin is behind the procedure:

$$4NH_4^+ + 6HCHO = (CH_2)_6N_4 + 4H^+ + 6H_2O$$

The produced acid is further titrated with the standard sodium hydroxide solution.

Procedure

Place 5 mL of formaldehyde solution and 1-2 drops of phenolphthalein into the conical flask. Keep adding 0.1 M sodium hydroxide solution dropwise with mixing until light-pink coloration appears. Then add an aliquot of the analyzed solution (10 mL) and mix the flask content. Keep the mixture for 1 min and then titrate it with the standard 0.1 M sodium hydroxide solution (precise concentration of 0.09570 M) until stable light-pink coloration appears. Repeat titrations as necessary.

Write down the titration results into the table, indicate the accepted volume of the consumed titrant and calculate the molar concentration of ammonium ions in the analyzed solution. Calculate and write down the mass (in g) of ammonium nitrogen and that of nitrate nitrogen in the analyzed solution.

Titration # 2. Determination of the total content of amide and ammonium nitrogen

The procedure is based on the oxidation of ammonium and amide nitrogen to elemental nitrogen by hypochlorite in the presence of potassium bromide in carbon(IV) oxide medium described by the hereunder total equations:

$$2NH_4^+ + 3ClO^- = N_2 + 3Cl^- + 2H^+ + 3H_2O$$

$$(NH_2)_2CO + 3ClO^- = CO_2 + N_2 + 2H_2O + 3Cl^-$$

The hypochlorite excess is further determined iodometrically:

$$ClO^- + 2I^- + 2H^+ = Cl^- + I_2 + H_2O$$

$$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$$

Procedure

Transfer an aliquot (5.00 mL) of the analyzed solution into the conical flask for titration, add 1 drop of methyl orange and 1-2 drops of 0.1 M HCl solution to attain the solution color change from orange to pink. Then add 5 mL of 8% $NaHCO_3$ solution and 5 mL of 8% KBr solution with the graduated test tube. Add 8.00 mL of hypochlorite solution from the burette under the fume hood. Mix the flask content, place the watch glass onto the flask and leave it for 10 min (use this time to carry out identification of individual fertilizers, see the next part). Then add 5 mL of 16% KI and 10 mL of H_2SO_4 (1:6, slowly!) with different graduated test tubes and mix the flask content once again. Place the watch glass onto the flask and leave it for 10 min. Titrate the liberated iodine with sodium thiosulfate solution till the solution color turns light-yellow ("straw-yellow"). Then add 2-3 drops of the starch solution and titrate under vigorous mixing (especially in case of precipitated iodine!) till stable disappearance of blue coloration. Repeat titration as necessary.

Carry out the blank experiment under the same conditions with the same amount of the reagents, but without the analyzed solution. **Attention: because of back titration, large volume of the titrant may be needed at this step (more than 25 mL).**. Repeat the titration as necessary. Ask your lab assistant for an additional portion of thiosulfate solution, if needed.

Write down the titration results into the table and calculate the total mass (in g) of carbamide and ammonium nitrogen in the analyzed solution.

Calculate the fractions (in %) of ammonium, nitrate, and carbamide nitrogen in the fertilizer under investigation.

Part 2. Qualitative analysis

The hereunder mineral fertilizers are placed in nine Eppendorf tubes (1 – 9):

- Phosphorite flour (calcium orthophosphate),
- Norway saltpeter (calcium nitrate),
- Ammonium saltpeter (ammonium nitrate),
- Ammonium sulfate,
- Potassium sulfate,
- Sylvinite (potassium chloride),
- Dolomite flour (calcium and magnesium carbonates),
- Monophosphate (potassium dihydrogen phosphate),
- Ammophos (ammonium hydrogen/dihydrogen phosphate).

Identify the fertilizers in the Eppendorf tubes using the set of the reagents provided. Fill in the table in the Answer sheets reporting your observations. Write down the corresponding reaction equations.

Part 3. Answer the <u>theoretical questions</u> in the Answer sheet.

Name		Country		Student's code	

ANSWER SHEETS

Part 1. Quantitative analysis

Titration # 1. Determination of the content of ammonium nitrogen

Burette reading, mL		Volume consumed for titration, mLл
V_1	V_2	V(NaOH)

The accepted volume of the titrant V(NaOH) = ______ mL.

Calculation:	
$c(NH_4^+)$ =	(M)
$m(N/NH_4^+)$ =	(g)
$m(N/NO_3^-)$ =	(g)

Titration # 2. Determination of the total content of amide and ammonium nitrogen

Burette reading, mL		Volume consumed for titration, mLл
V_1	V_2	$V(Na_2S_2O_3)$

The accepted volume of the titrant $V(Na_2S_2O_3)$ = ______ mL.

Name		Country		Student's code	

Burette reading, mL		Volume consumed for titration, mLл
V_1	V_2	$V(Na_2S_2O_3)$

The accepted volume of the titrant in the blank experiment $V_{ref}(Na_2S_2O_3)$ = ______ mL.

Calculation:

$m(N/NH_4^+) + m(N/NH_2CONH_2) =$ (g)

Calculate the content (in %) of nitrogen forms in the furtilizer

Calculation

Answer

Chemical form of nitrogen	% N
N/NH_4^+	
N/NO_3^-	
N/NH_2CONH_2	

Name		Country		Student's code	

Part 2. Qualitative analysis

Write down the reagents used in the reactions with the unknown samples in the upper line of the table. Write down your observations and reaction equations in the corresponding cells. Use the space under the table if you need additional space to write down reaction equations.

Номер образца		Reagents used					
	1						
	2						

Name | | Country | | Student's code | |

	3						
	4						
	5	`					
	6						

Name		Country		Student's code	

	7						
	8						
	9						

(Additional space for reaction equations)

Name | Country | Student's code

Based on the obtained results, write down the Eppendorf tube codes corresponding to each furtilizer.

Furtilizer	Formula	Eppendorf tube label (number)
Phosphorite flour	$Ca_3(PO_4)_2$	
Norway saltpeter	$Ca(NO_3)_2$	
Ammonium saltpeter	NH_4NO_3	
Ammonium sulfate	$(NH_4)_2SO_4$	
Potassium sulfate	K_2SO_4	
Sylvinite	KCl	
Dolomite flour	$CaCO_3$ / $MgCO_3$	
Monophosphate	KH_2PO_4	
Ammophos	$NH_4H_2PO_4$ / $(NH_4)_2HPO_4$	

Name		Country		Student's code	

3.Theoretical questions

1. Explain the role of KBr in the titration # 2? Write down the reaction schemes.

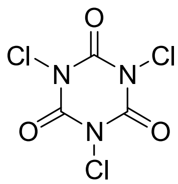
2. Overstated and poorly reproducible titrant volumes are obtained if too high concentration of sulfuric acid is used in iodometric titration. Propose a side process that may occur. Write down the reaction equation.

3. Chloramines are formed at incomplete oxidation of ammonia by hypochlorite. These compounds are responsible for unpleasant odor in swimming pools as well as for irritation of mucous membranes. Write down reaction equations of mono-, di-, and trichloramine formation and propose a method (write down the reaction equation) for chloramines (use dichloramine as an example) removal from swimming pool water.

4. Hypochlorite is decomposed when exposed to light (especially at direct sunlight). Write down the reaction equation.

Name		Country		Student's code	

5. Trichloroisocyanuric acid is used as a hypochlorite alternative for water disinfection:



Explain the action of trichloroisocyanuric acid (write down the corresponding reaction equation(s)).

6. Propose how to synthesize trichloroisocyanuric acid starting from inorganic salt(s).