36th IChO Practical Problems

- **safety rules** — follow them as in the preparatory problems described, in particular you have to wear safety goggles all the time, no eating or drinking is allowed in the lab.
- **violating safety rules** — you get one warning, offend again: you are out.
- **problem booklet** — 12 pages with 2 problems. Start with problem 1 and continue until a hint is given to start problem 2.
- **time** — 5 hours, 30 minutes warning before the end.
- **answer sheets:** — 3 pages
- **your name and student code** — write it on **every** answer sheet.
- **answers** — only in the appropriate boxes of the answer sheets, nothing else will be marked. Relevant calculations have to be shown.
- **use only the pen and calculator provided**
- **results** — the number of significant figures in numerical answers must conform to the rules of evaluation of experimental error. Mistakes will result in penalty points even if your experimental technique is flawless.
- **burette** — read it as accurately as possible.
- **more chemicals** — of Na_2EDTA, $Na_2S_2O_3$, superconductor solution, superconductor solid, polycarbonate or bisphenol A needed? Ask the instructor. You get a penalty of -5 points only for each of these extra chemicals.
- **questions** — concerning safety, apparatus, chemicals, organisation, toilet break: **ask your instructor.**
- **chemical waste** — only in the designated containers.
- **official English-language version** — **available** on request **for clarification only.** Ask the instructor.
- **after the stop signal** — put your answer sheets in the envelope (don't seal), deliver them at the appropriate instructor room. Keep the problem booklet together with the pen and calculator.

You must stop your work immediately after the stop signal has been given. A delay of 5 minutes will result in zero points for the current task.

Periodic table of elements

with atomic masses / u

1 **H** 1.01																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** 98.91	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.3	57-71	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.19	83 **Bi** 208.98	84 **Po** 208.98	85 **At** 209.99	86 **Rn** 222.02
87 **Fr** 223	88 **Ra** 226	89-103	104 **Rf** 261	105 **Db** 262	106 **Sg** 263	107 **Bh** 264	108 **Hs** 265	109 **Mt** 268									
			57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** 144.92	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
			89 **Ac** 227	90 **Th** 232	91 **Pa** 231	92 **U** 238	93 **Np** 237	94 **Pu** 244	95 **Am** 243	96 **Cm** 247	97 **Bk** 247	98 **Cf** 251	99 **Es** 252	100 **Fm** 257	101 **Md** 258	102 **No** 259	103 **Lr** 262

Apparatus

During the practical examination some of your glassware will have to be used more than once. Clean it carefully.
The hoods and the equipment within will also be used by several students. The numbers of your hood and of your instructor room is written on your bench.

apparatus	apparatus
2 beakers (100 mL)	1 heating plate with magnetic stirrer
1 beaker (weighed, labelled "beaker A")	1 magnetic stirring bar
1 beaker (weighed, labelled "beaker B")	3 melting-point tubes in a test tube (labelled "tube B")
1 beaker (400 mL)	1 measure for melting point tubes
1 pair of "rubber fingers" for handling hot beakers	1 Pasteur pipette (2 mL, grad.) with ball
1 bottle with dem. water (500 mL)	1 Peleus ball
2 brackets for condenser and flask	1 pipette (25 mL)
1 bracket for the burette with sleeve	1 plastic plug (NS 29)
1 burette (25 mL)	1 glass-ceramics (Ceran™) plate
1 suction filter (90 mm)	1 pair of protective glasses
1 condenser (NS 29)	1 role of pH paper
1 Erlenmeyer flask (100 mL, NS 29)	2 shards (2.5 cm x 2.5 cm)
4 Erlenmeyer flask (300 mL)	2 sleeves for the brackets
1 g fibreglass	1 spatula
6 filter papers for problem 1	1 micro spatula
6 filter papers for problem 2	2 stands
1 filter rack	1 suction bottle (500 mL) with ring
2 folded filter papers for problem 1	1 Teflon coupling (NS 29)
1 funnel for analysis ∅ = 80 mm	4 test tubes
1 funnel for liquids ∅ = 100 mm	1 test-tube rack
1 funnel for powder ∅ = 80 mm	1 volumetric flask (100 mL)
1 funnel for the burette	1 volumetric flask (250 mL)
2 glass rods 15 cm	75 cm glass tube
1 glass rod 21 cm	1 pair of tweesers
1 graduated cylinder (10 mL)	1 wiper
1 graduated cylinder (100 mL)	1 test-tube brush

Chemicals for each student

No	chemicals	formula	conc.	amount	R phrases	S phrases
1	polycarbonate (Makrolon)	-	solid	2.54 g	-	-
2	ethanol	C_2H_5OH	96 %	150 mL	11	7-16
3	hydrochloric acid	HCl	25 %	60 mL	36/37/38	26
4	sodium chloro acetate	$ClCH_2COONa$	solid	5 g	25-38-50	22-37-45-61
5	sodium hydroxide	NaOH	solid	4 g	35	26-37/39-45
6	sodium-hydroxide solution	NaOH	10%	100 mL	35	26-36/37/39-45
7	disodium-EDTA solution	Na_2-EDTA	0.1000 mol L^{-1}	100 mL	22-36/37/38	26-36
8	sodium acetate	CH_3COONa	solid	10 g	-	-
9	sodium-iodide solution	NaI	10 %	80 mL	-	22-24/25 *
10	sodium-thiosulfate solution	$Na_2S_2O_3$	0.01000 mol L^{-1}	100 mL	-	-

11	starch solution	-	-	20 mL	-	-
12	sulfuric acid	H_2SO_4	2 mol L^{-1}	50 mL	35	26-30-45
13	superconductor solution	$La_xM_{(2-x)}CuO_4$	-	-	22 [1)]	22-24/25 [1)]
14	superconductor solid	$La_xM_{(2-x)}CuO_4$	solid	250 mg	22	22-24/25
15	xylenol orange indicator	-	solid	500 mg	8	16-41
27	bisphenol A [2)]	$C_{15}H_{16}O_2$	solid		36/37/38-43	24-26-37
28	bisphenol A [3)]	$C_{15}H_{16}O_2$	solid		36/37/38-43	24-26-37

[1)] for the solid compound
[2)] will be handed out by the instructor on request during problem 1
[3)] will be handed out after the first step of problem 1 in the appropriate instructor room

Chemicals that have to be used in common (to be found in the hoods)

No	chemicals	formula	conc.		R phrases	S phrases
16	acetic acid	CH_3COOH	2 mol L^{-1}		10-35	23.2-26-45
17	ammonia solution	NH_3 (aq)	25 %		34-50	26-36/37/39-45-61
18	ammonium-carbonate solution	$(NH_4)_2CO_3$	2 mol L^{-1}		36/37/38 *	26-37/39 *
19	ammonium-oxalate solution	$(NH_4)_2C_2O_4$	0.25 mol L^{-1}		21/22 *	24/25 *
20	ammonium-sulfate solution	$(NH_4)_2SO_4$	1 mol L^{-1}		-	-
21	calcium-sulfate solution	$CaSO_4$	satur.		-	-
22	perchloric acid	$HClO_4$	10 %		34	23-26-36-45
23	potassium-dichromate solution	$K_2Cr_2O_7$	0.05 mol L^{-1}		43	24-37-45-60

* for the solid compound

Chemicals to perform a blank test which can be obtained from the instructor:

No	chemicals	formula	conc.		R phrases	S phrases
24	barium-chloride dihydrate	$BaCl_2 \cdot 2\ H_2O$	solid		20-25	45
25	calcium-chloride hexahydrate	$CaCl_2 \cdot 6\ H_2O$	solid		36	22-24
26	strontium-chloride hexahydrate	$SrCl_2 \cdot 6\ H_2O$	solid		-	22-24/25

Risk phrases (R)

R 8	Contact with combustible material may cause fire.
R 10	Flammable.
R 11	Highly flammable.
R 20	Harmful by inhalation.
R 22	Harmful if swallowed.
R 25	Toxic if swallowed.
R 34	Causes burns.
R 35	Causes severe burns.
R 36	Irritating to eyes.
R 37	Irritating to respiratory system.
R 38	Irritating to skin.
R 43	May cause sensitization by skin contact.
R 50	Very toxic to aquatic organisms.

Combination of risk phrases

R 21/22	Harmful in contact with skin and if swallowed.
R 36/37/38	Irritating to eyes, respiratory system and skin.

Safety phrases (S)

S 7	Keep container tightly closed.
S 16	Keep away from sources of ignition - No smoking.
S 22	Do not breathe dust.
S 23	Do not breathe gas/fumes/vapour/spray (appropriate wording to be specified by the manufacturer).
S 23.2	Do not breathe vapour.
S 24	Avoid contact with skin.
S 26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S 30	Never add water to this product.
S 36	Wear suitable protective clothing.
S 37	Wear suitable gloves.
S 41	In case of fire and/or explosion do not breathe fumes.
S 45	In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).
S 60	This material and its container must be disposed of as hazardous waste.
S 61	Avoid release to the environment. Refer to special instructions / Safety data sheets.

Combination of safety phrases (S)

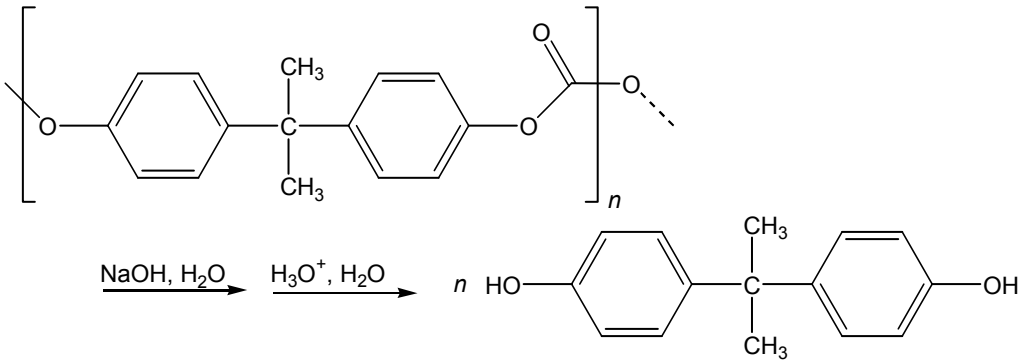
S 24/25	Avoid contact with skin and eyes.
S 36/37/39	Wear suitable protective clothing, gloves and eye/face protection.
S 37/39	Wear suitable gloves and eye/face protection.

1. Two-Step Organic Synthesis of 2,2-Bis(*p*-phenyleneoxyacetic acid)propane (Bisphenol A bis(carboxymethyl)ether)

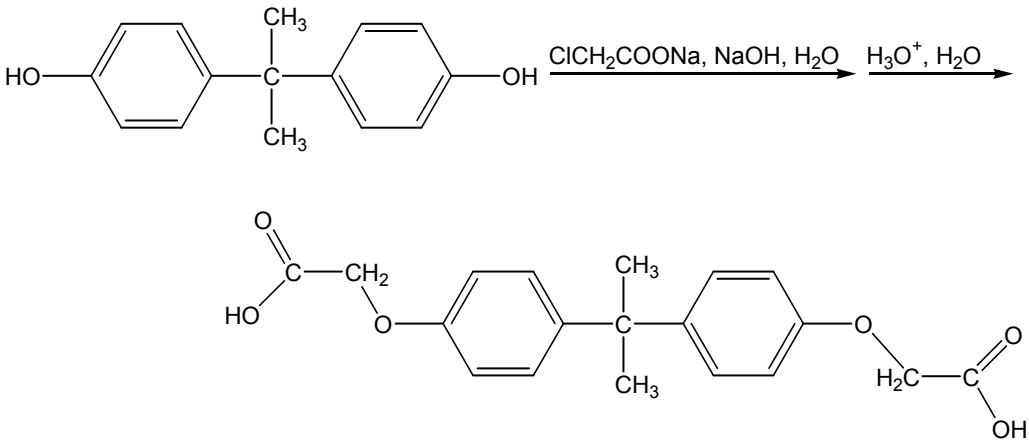
(100 points)

Introduction

In the first step the sodium salt of bisphenol A results as an intermediate from the alkaline hydrolysis of a polycarbonate. By adding an acid this salt is converted into the free 2,2-bis(4-hydroxyphenyl)propane (bisphenol A).



In the second step bisphenol A reacts with sodium chloroacetate to form the phenolic ether, bisphenol A bis(carboxymethyl)ether.



- In each step the product has to be isolated.
  (Drying and weighing will be done by the organizer.)
- For the product of step 2 three melting point tubes have to be filled.
  (Filling of the melting point tubes in step 1 will be done by the organizer.)
  (The melting points will be determined by the organizer.)
- When the organizer receives your labelled beaker A of step 1 you will get 2.00 g of bisphenol A as starting material for the second step.
- Answer the additional questions on the answer sheet **P1**.
- Do not remove the Ceran plate from the magnetic stirrer.

Procedures

Step 1 Preparation of bisphenol A by alkaline hydrolysis of a polycarbonate

Preparation:

- Put the pre-weighed 2.54 g of polycarbonate (No. **1**), 4.0 g of sodium hydroxide (No. **5**) and 3 mL of demineralized water into a 100 mL Erlenmeyer flask with ground-glass joint.
- Close the flask with a plastic plug and swirl it gently so that the solution does not contact the ground-glass joint. For aeration open the plastic plug occasionally. Strong heating can be observed, as the sodium hydroxide partially dissolves.
- Remove the plastic plug after swirling for about 4 minutes, add a magnetic stirring bar and put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Finally, add 20 mL of ethanol (No. **2**) through the condenser while stirring the reaction mixture.
- Heat the reaction mixture under reflux for 60 minutes. In the beginning adjust the thermostat of the heating plate to maximum. When the mixture starts boiling reduce the heat carefully, so that the mixture is kept under gentle reflux.
- A white precipitate is formed on heating.

During this waiting period you are highly advised to start working on the analytical chemistry experiment.

Isolation:

- Stop heating after one hour, allow the reaction mixture to cool down to ambient temperature, remove the condenser, add 25 mL of demineralized water and transfer the reaction mixture into a 400 mL beaker. Rinse the Erlenmeyer flask with 25 mL of demineralized water and add this to the contents of the beaker.
- Finally, fill up to 150 mL with demineralized water.
- If the reaction mixture is not clear, the mixture has to be filtered over fibre glass into an Erlenmeyer flask.
- Add slowly 15 mL of hydrochloric acid (No. **3**) stirring the mixture simultaneously with a glass rod. A rather oily or sometimes crystalline precipitate is formed.
- Ask your instructor for some seed crystals of bisphenol A (No. **27**) in order to accelerate the crystallization.
- Stir the reaction mixture thoroughly with the glass rod. For a quantitative crystallisation continue stirring from time to time till the supernatant aqueous solution is nearly clear.
- Collect the crude product by vacuum filtration, wash it twice with 10 mL portions of demineralized water and transfer it quantitatively into the tared and labelled beaker A.
- **For drying and weighing deliver your labelled beaker A into the instructor room.**
- Afterwards you will get a small jar filled with 2.00 g of bisphenol A (No. **28**), your starting material of the second step.

- On delivery of your product and on receipt of the starting material you have to sign. Even if you do not have any bisphenol A, please bring the empty beaker A to the instructors' room in order to get the starting material for step 2.

Step 2 Reaction of Bisphenol A with Chloroacetic Acid forming 2,2-Bis(*p*-phenyleneoxyacetic acid)propane (Bisphenol A bis(carboxymethyl)ether)

Preparation:

- Pour all the bisphenol A (No. **28**) you have received from the organizer when you had finished step 1 into a 100 mL Erlenmeyer flask with ground-glass joint.
- Add 10 mL of an aqueous sodium-hydroxide solution (No. **6**), 1 mL of demineralized water and a magnetic stirring bar.
- Put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Heat the reaction mixture with gentle stirring until a clear solution is formed.
- Remove the heating plate and the condenser and add 5.0 g of the sodium salt of chloroacetic acid (No. **4**) to the reaction mixture.
- After reconnecting the flask with the reflux condenser, heat the mixture to reflux with vigorous stirring for 30 min.
- Initially a clear solution is formed on heating. In some cases a colorless solid precipitates. If the complete mixture becomes solid in the course of the reaction, heating **must** be stopped.
- After that, 50 mL of ethanol (No. **2**) are added carefully through the condenser (beware of sudden boiling!). The mixture is stirred and heated under reflux for 5 minutes. A colourless solid precipitates, or the crystallisation which has already started is completed.

Isolation:

- After leaving it to cool down for 5 minutes, transfer the reaction mixture with another 50 mL of ethanol (No. **2**) quantitatively to a beaker. The reaction mixture should be stirred vigorously.
- The magnetic stirring bar is removed and the reaction mixture is filtered through a suction filter. Solids which separate in the filtrate are rejected. Rinse the beaker with 10 mL of ethanol (No. **2**). The precipitate is washed twice with 10 mL portions of ethanol (No. **2**). (The filtrate must be disposed of in the organic solvent waste!)
- Transfer the precipitate quantitatively into a beaker, add a stirring bar and dissolve it in 150 mL of demineralized water. The mixture must be stirred vigorously. Larger lumps of the solid must be crushed with the spatula.
- If the solution is not clear, it has to be filtered over a folded filter paper into an Erlenmeyer flask.

- The slow addition of 5 mL of hydrochloric acid (No. **3**) to the stirred reaction mixture results in the formation of a white precipitate.
- Collect the crude product by vacuum filtration, wash it twice with 10 mL portions of demineralized water and transfer it quantitatively into the tared and labelled beaker B.
- Take a small sample of the product with a micro spatula, crush it and dry it on a shard. Fill three melting point tubes with the homogenized, dried sample. For a close-packed and 5 mm high filling use the 75 cm glass tube and the measure.
- **Put all three melting point tubes into the test tube B, which is labelled with your student code, and give it together with your labelled beaker B with the product to the instructor. On delivery you have to sign.**

2. Qualitative and Quantitative Analysis of a Superconductor

(113 points)

Introduction

Superconductors based on lanthanum cuprate (La_2CuO_4) have the general composition of $La_xM_{(2-x)}CuO_4$ (M = Ca, Sr, Ba).

This problem consists of two parts:

- the qualitative determination of the alkaline earth metal(s)
- the quantitative determination of lanthanum and copper.

Read the burette as accurately as possible. Report your results on the answer sheets. Answer the additional questions and write the results with adequate accuracy.
The qualitative and quantitative parts of this experiment may be done in any order.

Procedures

2.1 Qualitative determination of the alkaline earth metal(s) (If the hood is occupied start with the titration 2.2)

In this experiment you have to use the superconductor as a solid ($La_xM_{(2-x)}CuO_4$; No. **14**).
At the beginning, lanthanum has to be separated as an insoluble residue.
All steps must be carried out in the hood!

Dissolve the complete sample in a beaker in about 5 mL of perchloric acid (No. **22**) by heating the mixture. Add 5 mL of demineralized water afterwards.
Cool down the solution until it is lukewarm.

Add about 5 mL of demineralized water and then ammonia solution (No. **17**), until the reaction mixture shows a basic reaction. Lanthanum precipitates as hydroxide and copper forms an intense blue-coloured tetraammine complex. The precipitate is filtered off and washed with a small amount of demineralized water.

An excess of ammonium-carbonate solution (No. **18**) is added to the filtrate and the mixture is being boiled for some minutes. The alkaline earth metal(s) will precipitate as carbonate(s). The precipitate is filtered off and washed a few times with a small amount of demineralized water.

Then, the precipitate is dissolved in acetic acid (No. **16**). Add sodium acetate (No. **9**) and an excess of potassium-dichromate solution (No. **23**). In the presence of barium, yellow $BaCrO_4$ precipitates. After boiling the mixture for one minute barium chromate is filtered off and washed with demineralized water.
(If there is no barium chromate precipitation, proceed in a way as if there were precipitation.)

Ammonia solution (No. **17**) is added to the clear filtrate until it is basic. Add an excess of ammonium-carbonate solution (No. **18**) and boil the mixture for some minutes. In the presence of strontium and/or calcium, white carbonate(s) precipitate(s).

The precipitate is filtered off and washed a few times with demineralized water.

Then it is dissolved in a mixture of about 2 mL of demineralized water and a few drops of hydrochloric acid (No. **3**). This solution is devided between two test tubes:

- Saturated calcium-sulfate solution (No. **21**) is added to one of the test tubes. In the presence of strontium a small amount of white strontium sulfate precipitates. To accelerate the precipitation, you can grind the inner surface of the test tube with a glass rod for a few minutes.
- Ammonium-sulfate solution (No. **20**) is added to the second test tube. In the presence of strontium and/or calcium, white sulfate(s) precipitate(s). The precipitate is filtered off and washed with a very small amount of demineralized water.
  1 mL of ammonium-oxalate solution (No. **19**) is added to the filtrate. In the presence of calcium, white calcium oxalate precipitates after a few minutes.

Preparation of the superconductor parent solution

There is a superconductor solution ($La_xM_{(2-x)}CuO_4$ in perchloric acid; No. **13**) in a volumetric flask.
Fill it up with demineralized water to a volume of 250.0 mL. From now on this solution is called “parent solution”.

2.2 Quantitative determination of the total content of lanthanum and copper

Transfer 25.00 mL of the parent solution into an Erlenmeyer flask.
Add about 5-6 piled spatula of sodium acetate (CH_3COONa; No. **8**) and 2 micro spatula of xylenol orange indicator (No. **15**) to this solution and make up with demineralized water to a volume of about 75 mL.
The pH-value has to be about **pH 6** before the determination, otherwise add more sodium acetate.
Titrate the solution with Na_2-EDTA solution (No. **7**). The color of the solution changes from light violet to intensely light-green. (In between, the color changes a few times.)

Repeat this procedure as many times as necessary.

2.3 Quantitative determination of the copper content

Transfer 25.00 mL of your parent solution (No. **13**) into the 100 mL volumetric flask and fill up with demineralized water to a volume of 100.0 mL.
For each titration, transfer 25.00 mL of this solution into an Erlenmeyer flask and add sodium hydroxide solution (No. **6**), until the solution shows an alkaline reaction. During this procedure, a blue precipitate forms. Add sulfuric acid (No. **12**) until the blue precipitate dissolves. The solution has to be acidic (**pH 1-2**) and will contain a small amount of a white precipitate.
Add 10 mL of sodium-iodide solution (No. **9**), and swirl the Erlenmeyer flask for about 1 minute. Titrate the solution with sodium-thiosulfate solution (No. **10**). Add some starch

solution (No. **11**) as an indicator just before the end of the titration. At the end, the solution has to be colourless for at least 60 seconds.

Repeat this procedure as many times as necessary.