

**University of Warsaw, Faculty of Chemistry
Department of Chemical Technology
Laboratory 'Utilization of pollution and waste'**

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Experiment
„Water treatment”

2013/2014

Konspekt - Ćw. 3 Uzdatnianie wody

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Czas w godzinach zegarowych

Wykon./ Czas	0,5h	1h	1,5h	2h	2,5h	3h	3,5h	4h
Asystent / studenci	Kolokwium wejściowe	Informacja i pomoc w sytuacjach jej wymagających Ciągła kontrola czynności wykonywanych przez studentów						
Studenci – praca na instalacji technologicznej	Regeneracja kationitu http://www.p://www	Odmywanie Kationitu http://www.chem.uw.edu.pl/people/AMyslinski/cw3/ok01.htm	Regeneracja anionitu http://www.c	Odm. anionitu http://www.chem.uw.edu.pl/people/AMyslinski/cw3/oa01.htm	Sorpccja i demineralizacja wody http://www.chem.uw.edu.pl/people/AMyslinski/cw3/sid.htm			
		Pobieranie próbek H ₂ O do analizy ChZT1 i zaw. Ca ²⁺	Neutr. ścieków	Sorpccja na C aktyw.	Pobieranie próbek H ₂ O do II analizy zaw. Ca ²⁺	Czas na posilek	Czas na posilek	
Studenci – praca na stanowisk. anal. instrum.			Kond_1	Kontr. neutr ~10 pom. pH	Kond_2	Pomiary kondunktancji wody zdemineralizowanej 40 - 60 pom. co ~20 cm ³		
Studenci – praca na stanowisk. analizy miareczk.		Anal. miana KMnO ₄	Analiza miana EDTA	Analiza ChZT1 Wody surowej	Analiza Ca ²⁺ H ₂ O surowej	Analiza ChZT2 Woda po sorpc.	Analiza Ca ²⁺ woda zdejon.	Próba Clarke
Studenci – praca przy komputerze	Start i log.	ster.	ster.	ster.	ster.	ster.	Wpisywanie wyników pomiaru konduktancji jako funkcji objętości wody zdemineralizowanej – pomiar objętości samoczynny	
Drukarka	Samoczynny wydruk protokołu ćwiczenia							

Preface

Exercise consists of two simultaneously performed actions: technological process and analysis.

Table of student tasks during experiment

The main technological operations	Titrimetric analysis	Instrumental analysis
<ol style="list-style-type: none"> 1. Login 2. Regeneration of Cation Resin 3. Cation resin stripping 4. Regeneration of anion resin 5. Anion resin stripping 6. Neutralization of liquid waste 7. Sorption and ion exchange 	<ol style="list-style-type: none"> 1. Determination of titers of solutions of KMnO_4 2. Determination of titers of solution of EDTA 3. Analysis of untreated water oxidisability 4. Analysis of Ca^{+2} ion content in untreated water 5. Analysis of treated water oxidisability 6. Analysis of Ca^{+2} ion content in treated water <hr/> <ol style="list-style-type: none"> 7. Clark analyzis 	<ol style="list-style-type: none"> 1. Conductometry #1 - untreated water 2. pH-metry of liquid waste 3. Conductometry #2 - treated water
Calculations		
<ol style="list-style-type: none"> 1. Entering data into the calculation program 2. Determine of ion exchange capacity of cation resin based on data obtained with deionized water conductivity as a function of its volume (homework) 		

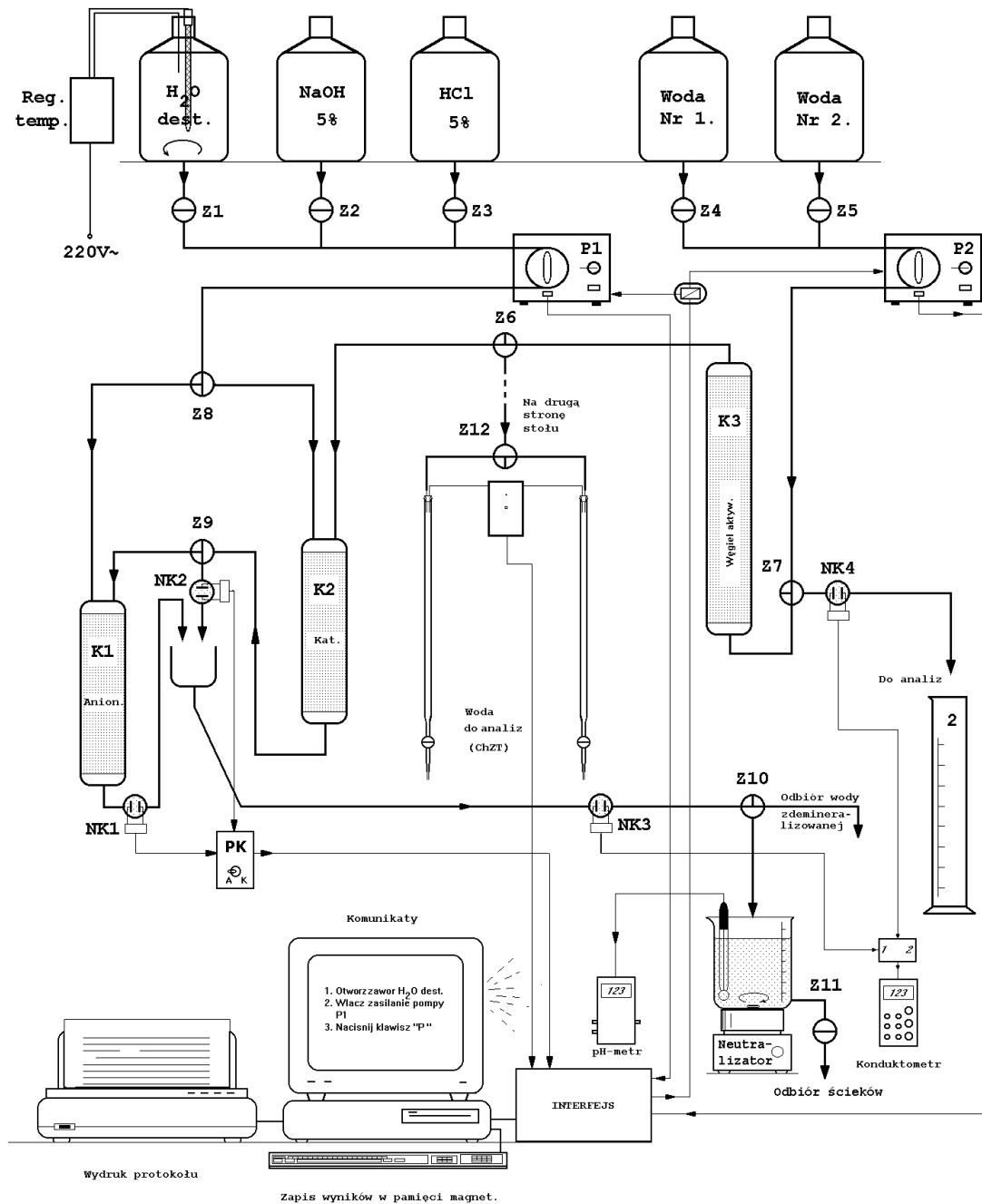
At the beginning you must log on to the computer, which is equivalent to the running process. After entering the date, students personal data, tasks, process parameters (speed of pumping water through the bed, kind of raw material, etc.) Afterwards computer prints exercise protocol header, and after that - as the work progresses - the protocol itself is supplemented by the results of measurements, the information the correct use of the apparatus, errors, etc.

On the screen, there are specific messages and commands that need to be performed. Messages are also repeated by the voice synthesizer, which frees practitioners from permanent monitor tracking during run-time analysis.

In the final phase of the exercise, using the keyboard, enter the results of the titration analysis, automatic conversion and print their results.

The technological process

Schematic diagram



Regeneration of ion exchangers and stripping of excess reagents

The first operation to be performed is the regeneration of ion exchange resins. Ionites work in hydrogen - hydroxide cycle. A 5% solution of hydrochloric acid is used to regenerate cation exchanger, and a 5% sodium hydroxide solution to anion exchange resin. Regeneration involves redrawing the appropriate solutions for the bed ion exchange resins in columns. After setting the appropriate valve, peristaltic pump pumps solutions to the columns. The eluate conductivity is controlled. The appearance of strong electrolyte solutions in the eluate testifies to the completion of the regeneration process.

Afterwards, remove excess regenerating solution remaining in the bed with warm distilled water. Water for washing is pumped from the tank with the same pump used for the regenerating solutions. The difference is in the relevant set of connecting valves.

The stripping provides a neutral pH of the eluate, and atrophy of electrical conductivity. Conductivity allows for accurate assessment of the condition and sends the information to the computer. The computer stops the operation when the conductivity of the eluate reaches a value of about $5 \mu\text{S} / \text{cm}$.

Neutralization of waste solutions

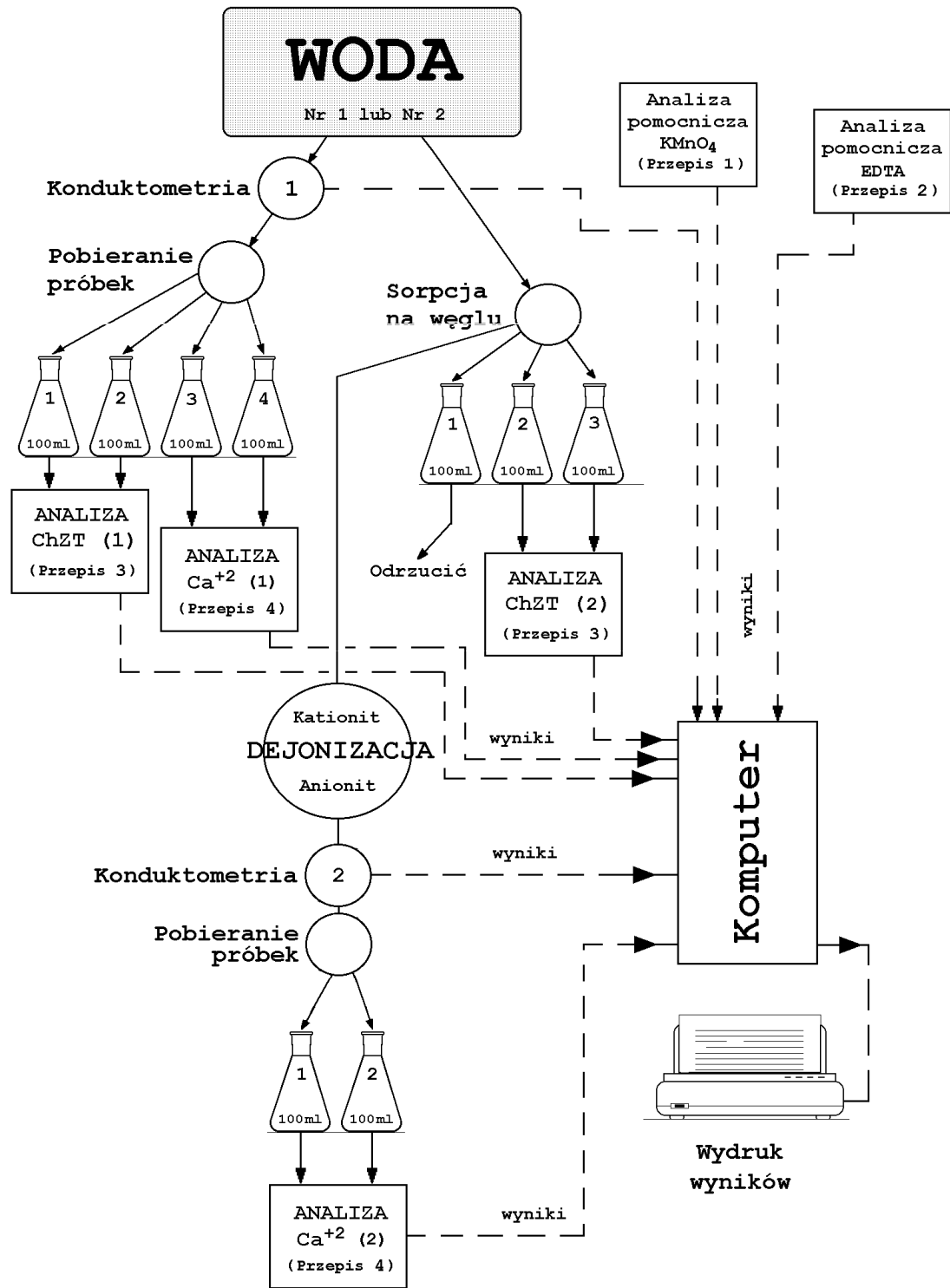
Regenerating and rinsing solutions, acid and alkali are neutralized in neutralizer. Their reaction is controlled by a pH meter. The computer reminds you of the periodic readings of pH in the wastewater. When the pH reaches a value of 6 - 8, recommend discharging of sewage (2 - 5% NaCl solution) into the sewer.

Water treatment

Treated water from the tank must be cleaned by running it through a column packed with activated carbon. Before treatment and after its execution, sample for determination of COD parameter. The exact procedure is given on a computer monitor. Schematic of analytical work shown in Figure 2.

Then, purified water should be directed to the cation exchange column, and thus the anionit column. The effluent from the anionit column flows to the conductivity sensor than to the receptacles. Water from the receptacles must be sampled to determine the residual hardness. At the same time should be carried out electrical conductivity measurements of treated water as a function of its volume. Also here, the computer signals the next measurement time and students introduce a result thru the keyboard. The increase in conductivity indicates the end of activity of bed ion exchanger. This will allow for subsequent appointments of the working exchange capacity of the column.

The rules are numbered according to the analytical scheme of the analytical work. Moving from top to bottom schema the students meets objects symbolize analytical work to be performed.



The rules developed analytical simplified versions on the basis of Polish Standards PN-85/045578/02 (COD) - resp. ISO 6058-1984 and PN-91/C-04551/01 (determination of calcium).

Recipe 1 - Determination of titre KMnO_4

1. To the two conical flasks with a capacity of 250 or 300 cm^3 pipette at 100.0 cm^3 of distilled water, then...
2. Measure out 10.0 cm^3 using a burette at 0.0125 N solution that is 0.0625 mol/dm^3 KMnO_4
3. Transfer the flask under the fume hood and ...
4. Twice measure out 10 cm^3 of H_2SO_4 (1 part by volume. Acid + 3 parts. vol. dest. water) using a measuring cylinder and pour the acid to the flasks. Acid & cylinder is under the hood.
5. Mix the contents of the flasks and put into the boiling water bath and heat for 30 minutes.
6. After removing the flask from the bath, transfer the flask on the table next to an automatic pipette and pipette as soon as possible 10.0 cm^3 0.0125 N, ie 0.025 mol/dm^3 solution of $(\text{COONa})_2$
7. Stir the contents of the flask and titrate the hot KMnO_4 until the creation of a very **weak pink color** persisting for 1 - 2 minutes, which indicates the titration end point. Record the results.
8. Re-add the following 10.0 cm^3 0.0125 N, ie 0.025 mol/dm^3 solution of $(\text{COONa})_2$ to the flasks, and again titrate to a very **weak pink color** persisting for 1 - 2 minutes.
9. Save KMnO_4 solution volume to the score sheet. Calculate the arithmetic mean of the two previous results.

Recipe 2 - Determination of titre of 0.01 mol of a solution of Na_2 [EDTA]

1. Pipette twice 10.0 cm^3 0.01 mol/dm^3 CaCl_2 solution (marked on the bottle as a Ca^{+2} 0.40 mg/cm^3) to the two conical flasks with a capacity of 200 - 300 cm^3 .
2. Add to the solution:
 - a) 100 cm^3 of distilled water (measured out the measuring cylinder)
 - b) 3 cm^3 of 24% KOH solution (measured out the measuring cylinder)
 - c) ~ 200 mg calces (indicator) - ie one spatula.
Mix the contents of the flask to dissolve the indicator.
3. Titrate a solution of Na_2 [EDTA] to change color from **pink** to **purple**. Excess titrant causes a color change to **blue** and shows on overtitration.
4. Note results in the score sheet, calculate the arithmetic mean.

Recipe 3 - Determination of water oxidisability untreated and treated water

1. Pipette (raw water) or measured by means of a burette (water after sorption) at 100.0 cm^3 of water to the two conical flasks with a capacity of $200 - 300 \text{ cm}^3$.
2. To the water add:
 - A) 10.0 cm^3 0.0125 N i.e. 0.0625 mol/dm^3 KMnO_4 solution, measured by means of a burette.
 - B) move the flasks and measure by means of a cylinder, add 10 cm^3 of H_2SO_4 located there.
3. Mix the contents of the flasks and put into the boiling water bath and heat for 30 minutes.
4. After removing the flask from the bath, transfer the flask on the table next to and immediately after them pipette 10.0 cm^3 of 0.0125 N , ie 0.025 mol/dm^3 solution of $(\text{COONa})_2$
5. Stir and titrate the hot contents with KMnO_4 until a **slightly pink color** persisting for 1 - 2 minutes.
6. Record the volume of KMnO_4 to a sheet of results. Consumption of KMnO_4 solution should be from 2 to 8 cm^3 . Unless this condition is not satisfied, repeat the determination using a sample of concentration adjusted accordingly.
7. Calculate the arithmetic mean of the results and enter to the worksheet.

Recipe 4 - Determination of concentration of Ca^{+2} ion

Preparation of the samples

1. Two samples of water at 100.0 cm^3 measured by pipette from the cylinder N^o. 2 pour into Erlenmeyer flasks with a capacity of $200 - 300 \text{ cm}^3$ and acidify with a few drops of nitric acid to pH 2 to indicator paper.
For Analysis 2 (after demineralization of water taken from the valve Z10) of water is not acidified.
2. For each sample:
 - a) Measure by means of a measuring cylinder approximately 20 cm^3 of triethanolamine to mask the ions of iron, aluminum and manganese. In case 2, this section analyzes omitted.
 - b) Pipette approximately 3 cm^3 of 24% KOH solution.
 - c) Measure by means of a spatula $\sim 200 \text{ mg}$ calces
3. Samples stir until completely dissolved calces.
4. A sample titrated with a solution Na_2 [EDTA] immediately to change color from **pink** to **purple**. Excess titrant causes a color change to **blue** and shows overtitration.
5. The final result marks the arithmetic mean of two determinations differing by no more than 5% as a result of the less amount.
6. Save the result in the score sheet.

ANALYSIS RESULTS SHEET

Exercise performed by:

1.
2.
3.

Number of treated water

Titration results:

N ^o .	COD _{Mn} (oxidisability)			Concentration of Ca ²⁺ ions		
	cm ³ 0.0125 n KMnO ₄ 1	cm ³ 0.0125 n KMnO ₄ 2	V = (1+2)/2	cm ³ 0.01 m. EDTA 3	cm ³ 0.01 m. EDTA 4	V = (3+4)/2
1. Titre of solutions						
2. Raw water.						
3. Treated water						

Warsaw, on.....2013.

Starting time:.....

End time:.....

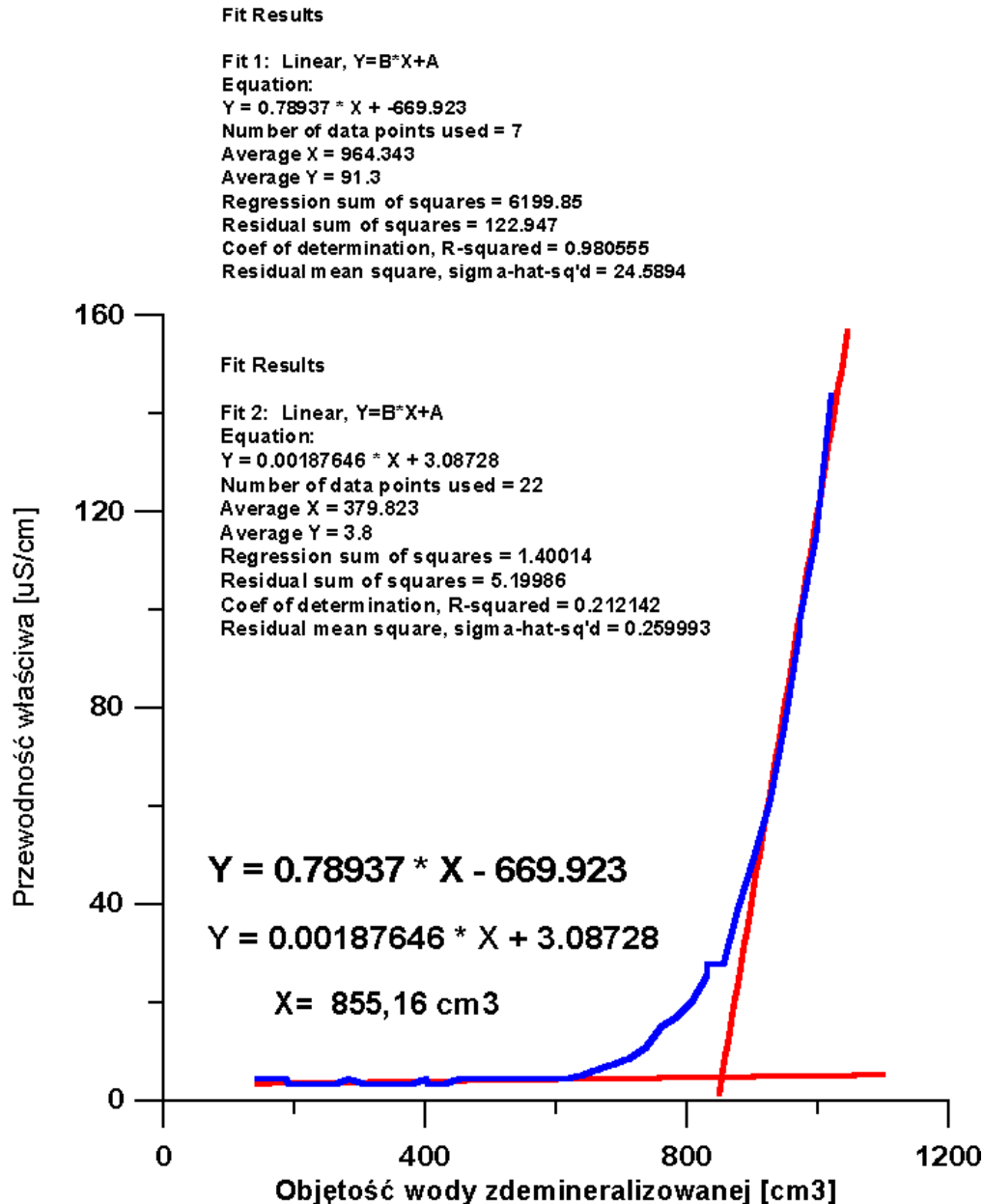
Signatures of students:

1.
2.
3.

Measurement of conductivity of deionized water

During the demineralization the computer calls for periodic measurements of conductivity (conductivity meter CC-411). The measurement results to be entered by keyboard. Exercise Protocol appears printed conductance depending on the volume of demineralized water.

Measuring the volume of water is carried out automatically by the delivery system: pump N° 2 - the computer. Printout is a source of data drawing from the graph of this dependence in the rectangular coordinate system. Please do it with of eg. Excel program. Data from the printout must be rewritten in spreadsheet rounding numbers to one decimal place.



X-axis – conductance; Y-axis – volume of demineralized water

The graph above shows a exemplary course of changes in conductance as a function of the volume of demineralized water. Using it should be designate a working exchange capacity of ion exchange columns.

The calculations and description of the exercises - activities that occur after the workshop (homework)

On the curve shown in the graph, you can extract two sections: a plateau when exchangers are fully active, and conductivity of deionized water maintained at a constant, low level (of a few $\mu\text{S} / \text{cm}$) and the rapid growth of conductivity illustrated by the increasing concentration of ions in the eluate. This indicates the state of depletion of ion exchange resins. Between them there is a transitional area.

If you assume that the flow rate of water through the column tends to zero $V \Rightarrow 0$, the shape of the curve would have two sections with one common point, the point of intersection.

In practice, the curve takes the shape as in the graph, you can also designate the point. For this purpose, draw two straight lines (Excel calls it "trend lines") for the highlighted sections above the curve, extend them until they intersect, and the X coordinate of the point of intersection is considered a known volume of water corresponding to the initial hardness of the working capacity of resin.

More on linear regression, you can read for example here:

http://en.wikipedia.org/wiki/Linear_regression

$y = a_1x + b_1$
 $y = a_2x + b_2$
 $x = \frac{b_2 - b_1}{a_1 - a_2}$

Excel allows you to perform these operations and equations for the simple determination of the form $y = ax + b$. Since the value of both functions at the point of intersection is the same, you can determine the value of x from these equations. When you use MS Excel measurement data should be initially divided into two parts corresponding to the straight line (plateau) and the straight line rapidly growing, and then generate trend lines for each of them. Finally show linear equations describing the trend lines.

The volume of x multiplied by the initial concentration of ions in the untreated water and the demineralization % efficiency can result in the form of their mass, and divided by the mass unit used in ion exchange resins - exchange capacity. In our case we take into account the mass of the cation, as we analyze the Ca^{+2} cations. In a more universal way exchange capacity can be expressed in [mval / g] by dividing the above result by 20.04 (40.08 - molar mass of the ion divided by 2 - valency of calcium). We must be aware that the actual working capacity is greater, because in addition to calcium cations in the water contained magnesium cations, sodium, iron, manganese, etc.

Working exchange capacity allows you to specify the volume of water of known ion content, which can be deionized without compromising the quality of the obtained product, and then start the auxiliary operations: regeneration and stripping of excess reactants.

To calculate the ion exchange capacity of working, you can use MS Excel spreadsheet available at:

http://www.chem.uw.edu.pl/people/AMyslinski/nowy/zarzadzanie_01/zdolnosc_01.xls

and read the result. Browser based system Mozilla (Firefox, Netscape) do not display correctly this window. Launch separately MS Excel spreadsheet.

The description should start with a header by the following formula:

Report on Experiment	Date of this exercise
Instructor: Adam Myśliński, MSc	Date of sending report:
The names of student(s):	Group number:
Experiment title: Water treatment	Instructor's remarks:

Content of the description should include:

1. Purpose of the experiment.
2. Literature studied on the experiment.
3. Theoretical basis of the experiment.
4. Description of the experiment, including:
 - a) block (simplified) diagram of the apparatus.
 - b) a list of reactants and reagents
 - c) the tasks accomplished.
 - d) observations and measurements.
4. Production of results:
 - a) the reaction equation,
 - b) the development of accounting results.
 - c) sources of error,
- 6) Discussion of the results.
- 7) Applications (among other things, whether the purpose of exercise is reached).

Description must be delivered to the instructor, not later than two weeks from the date of execution of the exercise.

The form of description - the file in MS Office Word (*.doc or *.rtf or *.docx) should be sent as an attachment at: admys@chem.uw.edu.pl