### CHEMISTRY: ART, SCIENCE, FUN



# PRACTICAL EXAMINATION

SOLUTION and GRADING SCHEME

JULY 18, 2007 MOSCOW, RUSSIA

### Problem 1. Ion-exchange chromatography of amino acids.

**1.1a** 3 marks for each peak if at least two blank wells between peaks 9 marks maximum.

### 1.1b Not graded.

**1.1.c** 1 point for each proper choice. Combined mixtures should include all fractions identified as "2" and "3" and should be free of fractions without amino acids. Fractions identified as "1" may be or may be not included.

3 marks maximum.

### 1.2-1.3

Content of an amino acid = 
$$\frac{A_{\lambda} \cdot n \cdot V \cdot M_{W}}{\varepsilon \cdot l}$$
,

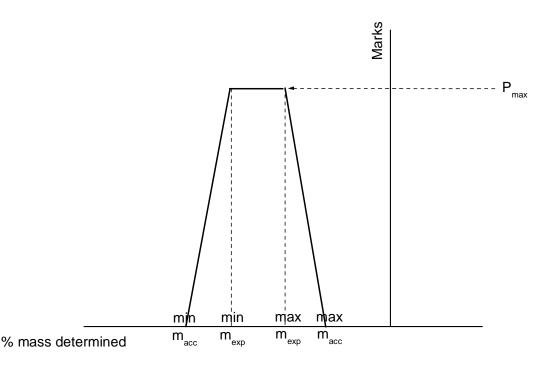
 $A_{\lambda}$  is the absorbance of the sample calculated from the spectra, l is the optical length (1.0 cm), n is the dilution factor determined as a ratio of the aliquot of analyzing solution (0.1 mL) and the final volume of the sample in the cuvette, V is the volume of the combined fraction from the corresponding peak, and  $M_W$  is the molar mass of the amino acid.

3 marks for correct formula,

3 marks for correct determination of optical densities (1 mark for each assay)

1 mark penalty for miscalculation.

Content of each amino acid is determined by using the following plot (values recalculated from volumes reported by students and absorbance values recorded by spectrophotometer)



Scoring:

$$m < min \ m_{acc} \ OR \ m > max \ m_{acc}$$

$$min \ m_{acc} < m < min \ m_{exp}$$

$$P_{\text{max}} \frac{(m - \min m_{acc})}{(\min m_{\text{exp}} - \min m_{acc})} \text{ marks}$$

$$min \ m_{exp} < m < max \ m_{acc}$$

Amino acid	Min	Min	Max	Max	P <sub>max</sub>
	m <sub>acc</sub> /m <sub>exact</sub> ·100%	m <sub>exp</sub> /m <sub>exact</sub> -100%	m <sub>exp</sub> /m <sub>exact</sub> -100%	m <sub>acc</sub> /m <sub>exact</sub> -100%	
Cys	70%	85%	110%	115%	22
His	60%	85%	110%	115%	22
Arg	25%	45%	65%	85%	22

### 72 marks maximum

**1.4** As it is given in the task text, mixed disulfide and 2-thio-5-nitrobenzoic acid are formed in the reaction.

Under slightly alkaline conditions, thiol group of (II) dissociates, and thiophenolate-anion is formed. Resonance structures can be realized for this compound:

The electronic structure of asymmetrical disulfide (I) does not differ considerably from that of the original Ellmann reagent. Therefore, it can be concluded that the compound responsible for coloration is thiophenolate-anion (a form containing C=S bond).

- 2 marks for three correct ionized structures, one of which contains C=S bond
- 1 mark for three other structures, all without C=S bond
- 1 mark for less than three structures, one of which contains C=S bond.
- 2 marks maximum.

## Problem 2. Determination of carbonate and hydrogen phosphate in an abrasive sample.

**2.1a, 2.2, 2.3** The values of the final volumes  $V_{1,f}$ ,  $V_{2,f}$ , and  $V_{3,f}$ , (as reported in the Answer Sheet) are graded according to the following scheme:

$$\Delta V = |V_{\text{reported}} - V_{\text{true}}|,$$

 $V_{\text{reported}}$  is either  $V_{1,f}$ ,  $V_{2,f}$ , and  $V_{3,f}$ ,  $V_{\text{true}}$  is the corresponding master value (will be given with the copies of students' works).

Value of $\Delta V$	Marks
$\Delta V \leq \Delta V_{\text{expected}}$	25
$\Delta V \geq \Delta V_{ m acceptable}$	0
$\Delta V_{ m expected} \leq \Delta V \leq \Delta V_{ m acceptable}$	$25 \times \left( \frac{\Delta V_{acceptable} - \Delta V}{\Delta V_{acceptable} - \Delta V_{\text{exp}ected}} \right)$

The values of  $\Delta V_{\text{expected}}$  and  $\Delta V_{\text{acceptable}}$  (in mL) are listed in the table below.

	$\Delta V$ , mL	
	expected	acceptable
$V_{1,\mathrm{f}}$	0.10	0.25
$V_{2,\mathrm{f}}$	0.15	0.40
$V_{3,\mathrm{f}}$	0.15	0.40

### 25 marks maximum for each titration

### **2.1b** Calculation of NaOH concentration

Your work 
$$c(\text{NaOH}) = \frac{c(HCl) \times V(HCl) \times V(aliquot)}{V(flask) \times V(NaOH)} = \frac{1.214 \ (mol/L) \times 10.00 (mL) \times 10.00 (mL)}{100.0 (mL) \times V_{1,f} \ (mL)} = \frac{c(\text{NaOH}) = \underline{\qquad} \quad \text{mol/L}$$

### **2.4** Calculation of the mass of $CO_3^{2-}$

Your work
$$m(\text{CO}_3^{2-}) (g) = \\ M(\text{CO}_3^{2-}) \times 1/2 \times \frac{c(NaOH) \times (V_{1,f} - V_{3,f}) \times V(flask)}{V(aliquot)} = \\ = 60.01 (g/mol) \times 1/2 \times \frac{c(NaOH) (mol/L) \times (V_{1,f} - V_{3,f}) (mL) \times 100.0 (mL)}{10.00 (mL)} \times 0.001 (L/mL) = \\ = \\ m(\text{CO}_3^{2-}) = \underline{\qquad} g$$

**2.5** Calculation of the mass of  $HPO_4^{2-}$ 

Your work
$$m(\text{HPO}_4^{2^-})(g) =$$

$$= M(\text{HPO}_4^{2^-}) \times \frac{c(NaOH) \times (V_{3,f} - V_{2,f}) \times V(flask)}{V(aliquot)} =$$

$$= 95.98 (g/mol) \times \frac{c(NaOH) (mol/L) \times (V_{3,f} - V_{2,f}) (mL) \times 100.0 (mL)}{10.00 (mL)} \times 0.001 (L/mL) =$$

$$= m(\text{HPO}_4^{2^-}) = \underline{\qquad} g$$

#### 2.1b, 2.4, 2.5

Correctness of calculations is graded by:

- 1) comparing the numerical result (including the number of significant figures) reported by a student with that obtained from the student's data using correct method of calculation;
- 2) checking out the a student's way of calculation.

5 marks maximum for completely correct calculation of each value

Penalty for errors in calculations or data presentation.

	Error type	Penalty marks (for calculation of each value)
1	Incorrect method of calculation	-5
2	Mistakes in dilution factor	-1
3	Confusion between units of measurement	-1
4	Mistake in stoichiometric (equivalency) relationships	-1
5	More or less than 4 significant figures in $c(NaOH)$	-0.5*
6	More than 4 or less than 3 significant figures in $m(CO_3^{2-})$ and $m(HPO_4^{2-})$	-0.5*
7	Rounding errors affecting the 1 <sup>st</sup> or 2 <sup>nd</sup> significant figures in the final result	-0.5**
8	8 Miscalculations and slips -0.2 pe	

<sup>\*</sup>Only the number of significant figures in the final answer is taken into account.

2.6a  

$$Ca^{2^{+}} + H_{2}PO_{4}^{-} \rightarrow CaHPO_{4} + H^{+}$$
  
or  
 $3Ca^{2^{+}} + 2HPO_{4}^{2^{-}} \rightarrow Ca_{3}(PO_{4})_{2} + 2H^{+}$ 

In course of these processes free protons evolve influencing the results of titration.

1 mark if the Answer Sheet contains at least one correct reaction equation. Incorrect equations are not penalized.

<sup>\*\*</sup>Not applied if the error originates from insufficient number of significant figures in previously calculated c(NaOH). No double penalty!

	Error	
Mistake	$CO_3^{2-}$	HPO <sub>4</sub> <sup>2-</sup>
	content	content
Below pH 4.5 (first endpoint, V <sub>2</sub> ) H <sub>2</sub> CO <sub>3</sub> is not titrated		
Between pH 4.5 and 10 (second endpoint, V <sub>3</sub> ) H <sub>2</sub> CO <sub>3</sub> is titrated	-	+
Thus, increase of $V_3$ ; $V_1$ and $V_2$ unchanged		
No influence, C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> is too weak base	0	0
Increase of $V_1$ and proportional decrease of $c(NaOH)$ [as		
$c(NaOH)V_1$ is equivalent to the initial amount of standard HCl	-	-
and so remains constant]; V <sub>2</sub> and V <sub>3</sub> unchanged		
Losses of sample leads to proportional decrease of V <sub>2</sub> and V <sub>3</sub>		
and therefore V <sub>3</sub> -V <sub>2</sub> ; V <sub>1</sub> unchanged	+	_
Increase of V <sub>2</sub> , V <sub>1</sub> and V <sub>3</sub> unchanged	0	_
Increase of V <sub>3</sub> , V <sub>1</sub> and V <sub>2</sub> unchanged	-	+