

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

$$\text{Content of an amino acid} = \frac{A_{\lambda} \cdot n \cdot V \cdot M_w}{\epsilon \cdot l},$$

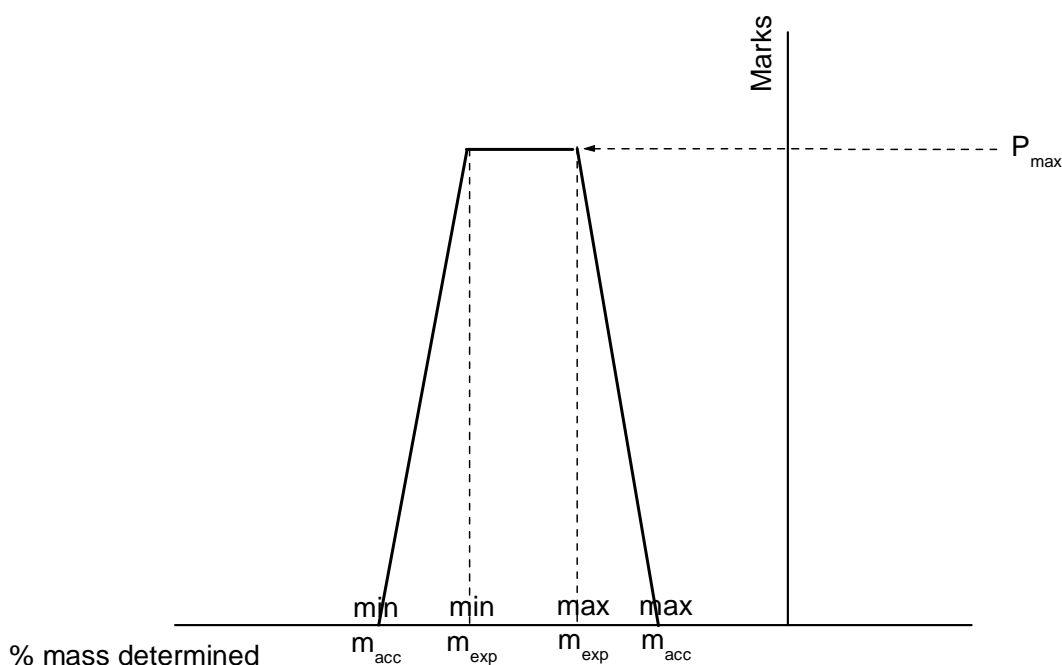
A_{λ} is the absorbance of the sample calculated from the spectra, l is the optical length (1.0 cm), n is the dilution factor determined as a ratio of the aliquot of analyzing solution (0.1 mL) and the final volume of the sample in the cuvette, V is the volume of the combined fraction from the corresponding 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 $m > \max m_{acc}$

0 marks

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

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

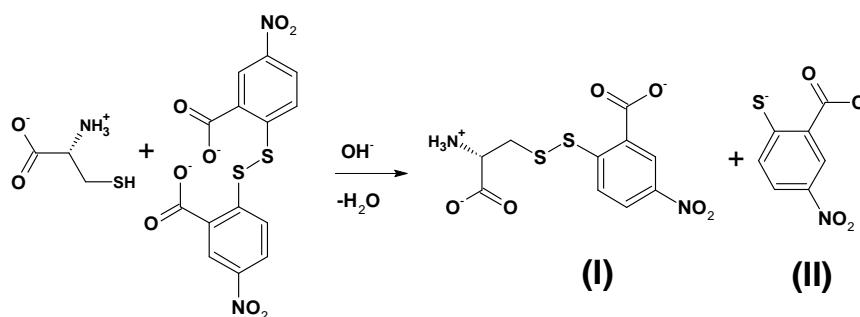
$\min m_{exp} < m < \max m_{acc}$

P_{max} marks

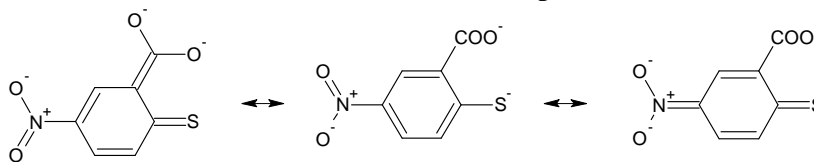
Amino acid	Min m_{acc}/m_{exact} ·100%	Min m_{exp}/m_{exact} ·100%	Max m_{exp}/m_{exact} ·100%	Max m_{acc}/m_{exact} ·100%	P_{max}
Cys	70%	85%	110%	115%	22
His	60%	85%	110%	115%	22
Arg	25%	45%	65%	85%	22

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

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

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

	ΔV , mL	
	expected	acceptable
$V_{1,f}$	0.10	0.25
$V_{2,f}$	0.15	0.40
$V_{3,f}$	0.15	0.40

25 marks maximum for each titration

2.1b Calculation of NaOH concentration

Your work

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

=

$$c(\text{NaOH}) = \underline{\hspace{2cm}} \text{ mol/L}$$

2.4 Calculation of the mass of CO_3^{2-}

Your work

$$m(\text{CO}_3^{2-}) (\text{g}) =$$

$$M(\text{CO}_3^{2-}) \times 1/2 \times \frac{c(\text{NaOH}) \times (V_{1,f} - V_{3,f}) \times V(\text{flask})}{V(\text{aliquot})} =$$

$$= 60.01 (\text{g/mol}) \times 1/2 \times \frac{c(\text{NaOH}) (\text{mol/L}) \times (V_{1,f} - V_{3,f}) (\text{mL}) \times 100.0 (\text{mL})}{10.00 (\text{mL})} \times 0.001 (\text{L/mL}) =$$

=

$$m(\text{CO}_3^{2-}) = \underline{\hspace{2cm}} \text{ g}$$

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

Your work

$$\begin{aligned}
 m(\text{HPO}_4^{2-}) \text{ (g)} &= \\
 &= M(\text{HPO}_4^{2-}) \times \frac{c(\text{NaOH}) \times (V_{3,f} - V_{2,f}) \times V(\text{flask})}{V(\text{aliquot})} = \\
 &= 95.98 \text{ (g/mol)} \times \frac{c(\text{NaOH}) \text{ (mol/L)} \times (V_{3,f} - V_{2,f}) \text{ (mL)} \times 100.0 \text{ (mL)}}{10.00 \text{ (mL)}} \times 0.001 \text{ (L/mL)} = \\
 &= \\
 & \qquad \qquad \qquad m(\text{HPO}_4^{2-}) = \underline{\hspace{2cm}} \text{ g}
 \end{aligned}$$

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

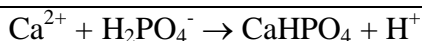
Penalty for errors in calculations or data presentation.

	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 $c(\text{NaOH})$	-0.5*
6	More than 4 or less than 3 significant figures in $m(\text{CO}_3^{2-})$ and $m(\text{HPO}_4^{2-})$	-0.5*
7	Rounding errors affecting the 1 st or 2 nd significant figures in the final result	-0.5**
8	Miscalculations and slips	-0.2 per error

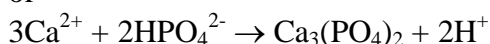
* Only the number of significant figures in the final answer is taken into account.

** Not applied if the error originates from insufficient number of significant figures in previously calculated $c(\text{NaOH})$. **No double penalty!**

2.6a



or



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.

2.6b

Mistake	Error	
	CO ₃ ²⁻ content	HPO ₄ ²⁻ content
Below pH 4.5 (first endpoint, V ₂) H ₂ CO ₃ is not titrated Between pH 4.5 and 10 (second endpoint, V ₃) H ₂ CO ₃ is titrated Thus, increase of V₃ ; V₁ and V₂ unchanged	-	+
No influence, C₂O₄²⁻ is too weak base	0	0
Increase of V₁ and proportional decrease of c(NaOH) [as c(NaOH)V ₁ is equivalent to the initial amount of standard HCl and so remains constant]; V₂ and V₃ unchanged	-	-
Losses of sample leads to proportional decrease of V₂ and V₃ and therefore V₃-V₂; V₁ unchanged	+	-
Increase of V₂, V₁ and V₃ unchanged	0	-
Increase of V₃, V₁ and V₂ unchanged	-	+