2010 U. S. NATIONAL CHEMISTRY OLYMPIAD

NATIONAL EXAM – PART III

Prepared by the American Chemical Society Olympiad Laboratory Practical Task Force

OLYMPIAD LABORATORY PRACTICAL TASK FORCE

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DIRECTIONS TO THE EXAMINER–PART III

The laboratory practical part of the National Olympiad Examination is designed to test skills related to the laboratory. Because the format of this part of the test is quite different from the first two parts, there is a separate, detailed set of instructions for the examiner. This gives explicit directions for setting up and administering the laboratory practical.

There are two laboratory tasks to be completed during the 90 minutes allotted to this part of the test. Students do not need to stop between tasks, but are responsible for using the time in the best way possible. **Each procedure must be approved for safety by the examiner before the student begins that procedure.**

Part III	**2 lab problems**	**laboratory practical**	**1 hour, 30 minutes**

Students should be permitted to use non-programmable calculators.

DIRECTIONS TO THE EXAMINEE–PART III

DO NOT TURN THE PAGE UNTIL DIRECTED TO DO SO. WHEN DIRECTED, TURN TO PAGE 2 AND READ THE INTRODUCTION AND SAFETY CONSIDERATIONS CAREFULLY BEFORE YOU PROCEED.

There are two laboratory-related tasks for you to complete during the next 90 minutes. There is no need to stop between tasks or to do them in the given order. Simply proceed at your own pace from one to the other, using your time productively. You are required to have a procedure for each problem approved for safety by an examiner before you carry out any experimentation on that problem. You are permitted to use a non-programmable calculator. At the end of the 90 minutes, all answer sheets should be turned in. Be sure that you have filled in all the required information at the top of each answer sheet. **Carefully follow all directions from your examiner for safety procedures and the proper disposal of chemicals at your examining site.**

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ABBREVIATIONS AND SYMBOLS					
amount of substance	*n*	Faraday constant	*F*	molar	M
ampere	A	free energy	*G*	molar mass	*M*
atmosphere	atm	frequency	ν	mole	mol
atomic mass unit	u	gas constant	*R*	Planck's constant	*h*
Avogadro constant	N_A	gram	g	pressure	*P*
Celsius temperature	°C	hour	h	rate constant	*k*
centi– prefix	c	joule	J	reaction quotient	*Q*
coulomb	C	kelvin	K	second	s
density	d	kilo– prefix	k	speed of light	*c*
electromotive force	*E*	liter	L	temperature, K	*T*
energy of activation	E_a	measure of pressure	mm Hg	time	*t*
enthalpy	*H*	milli– prefix	m	vapor pressure	
entropy	*S*	molal	*m*	VP	
equilibrium constant	*K*			volt	V
				volume	*V*

CONSTA

R = 8.314 J·mol

R = 0.0821 L·atm·mol^{-}

1 F = 96,500 C·mol^{-1}

1 F = 96,500 J·V^{-1}·mol^{-1}

$N_A = 6.022 \times 10^{23}$ mol^{-1}

$h = 6.626 \times 10^{-34}$ J·s

$c = 2.998 \times 10^{8}$ m·s^{-1}

0 °C = 273.15 K

PERIODIC TABLE OF THE ELEMENTS

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** 1.008																	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											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)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57 **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227)	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (264)	108 **Hs** (277)	109 **Mt** (268)	110 **Ds** (281)	111 **Rg** (272)	112 Uub (277)	113 (Uut)	114 (Uuq)	115 (Uup)	116 (Uuh)	117 (Uus)	118 (Uuo)

58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	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)

2010 U. S. NATIONAL CHEMISTRY OLYMPIAD
PART III – LABORATORY PRACTICAL

Student Instructions

Introduction

These problems test your ability to design and carry out laboratory experiments and to draw conclusions from your experimental work. You will be graded on your experimental design, on your skills in data collection, and on the accuracy and precision of your results. Clarity of thinking and communication are also components of successful solutions to these problems, so make your written responses as clear and concise as possible.

Safety Considerations

You are required to wear approved eye protection and gloves at all times during this laboratory practical. You also must follow all directions given by your examiner for dealing with spills and with disposal of wastes. In particular, special precautions are required when using the silver nitrate solution in Problem #2. Do not get it on your skin or clothing as it will cause stains. Please wash off any chemicals spilled on your skin or clothing with large amounts of tap water. On Problem #2, neither solution '$AgNO_3$ solution' nor 'K_2CrO_4 solution' can be disposed of down the drain. Both solutions need waste beakers (provided) in which the used pipettes should be placed.

Lab Problem 1

You have been given a well plate, several test tubes and pipets, a concentrated ammonia solution, access to distilled water, and four numbered vials containing iron (III) chloride hexahydrate, cobalt (II) sulfate heptahydrate, copper (II) chloride dihydrate, and potassium oxalate monohydrate, though not necessarily in this order. Devise and carry out an experiment to produce at least FIVE new different complex compounds, using your understanding of coordination compound geometry and qualitative evidence in your results.

Lab Problem 2

You have been given a sample of seawater, a pipet that contains 5.0×10^{-4} mole/gram $AgNO_3$, a pipet that contains $K_2CrO_4(aq)$, several small test tubes, and access to an electronic balance. Devise and carry out an experiment to determine the percentage of chloride ion, $Cl^-(aq)$, in seawater.

K_{sp} at 25 °C
$AgCl = 1.77 \times 10^{-10}$
$Ag_2CrO_4 = 1.12 \times 10^{-12}$

Answer Sheet for Laboratory Practical **Problem 1**

Student's Name: ______________________________

Student's School:______________________ **Date:** ______________

Proctor's Name: ______________________________

ACS Section Name:__________________ **Student's USNCO test #:** ________

1. Give a brief description of your experimental plan.

2. Data and Observations.

Vials	Contents as correctly written formulas	Evidence
#1		
#2		
#3		
#4		

Before beginning your experiment, you must get Approval (for safety reasons) from the examiner **Examiner's Initials:**

3. Show any relevant reactions and sketch the possible geometry of each formed compounds.

4. Conclusions

Reactant(s) Used	Proposed coordinate complex formula	Evidence

Answer Sheet for Laboratory Practical **Problem 2**

Student's Name: ____

Student's School: ______________________________ **Date:** ________________

Proctor's Name: ____

ACS Section Name: ______________________ **Student's USNCO test #:** __________

1. Give a brief description of your experimental plan.

2. Record your data and all relevant balanced chemical equations.

Before beginning your experiment, you must get Approval (for safety reasons) from the examiner	**Examiner's Initials:**

3. Calculations:

4. Conclusion. The percentage of chloride ion present in seawater =

5. List the assumptions that you made in this experiment:

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NATIONAL EXAM—PART III

Prepared by the American Chemical Society Olympiad Laboratory Practical Task Force

Examiner's Instructions

Directions to the Examiner:

Thank you for administering the 2010 USNCO laboratory practical on behalf of your Local Section. It is essential that you follow the instructions provided, in order to insure consistency of results nationwide. There may be considerable temptation to assist the students after they begin the lab exercise. It is extremely important that you do not lend any assistance or hints whatsoever to the students once they begin work. As in international competition, the students are not allowed to speak to anyone until the activity is complete.

The equipment needed for each student for both lab exercises should be available at his/her lab station or table when the students enter the room. The equipment should be initially placed so that the materials used for Lab Problem 1 are separate from those used for Lab Problem 2.

After the students have settled, read the following instructions (in italics) to the students.

Hello, my name is ________ . Welcome to the lab practical portion of the U.S. National Chemistry Olympiad Examination. In this part of the exam, we will be assessing your lab skills and your ability to reason through a laboratory problem and communicate its results. Do not touch any of the equipment in front of you until you are instructed to do so.

You will be asked to complete two laboratory problems. All the materials and equipment you may want to use to solve each problem has been set out for you and is grouped by the number of the problem. You may use equipment from one problem to work on the other problem, but the suggested ideal equipment and chemicals to be used for each problem has been grouped for you. You will have ***one hour and thirty minutes*** *to complete the* ***two problems****. You may choose to start with either problem. You are required to have a procedure for each problem approved for safety by an examiner. (Remember that approval does not mean that your procedure will be successful – it is a safety approval.) When you are ready for an examiner to come to your station for each safety approval, please raise your hand.*

Safety is an important consideration during the lab practical. ***You must wear goggles and gloves at all times.*** In particular, s*pecial precautions are required when using the silver nitrate solution in Problem #2. Do not get it on your skin or clothing as it will cause stains. Please wash off any chemicals spilled on your skin or clothing with large amounts of tap water. On Problem #2, neither solution '*$AgNO_3$ *solution' nor '*K_2CrO_4 *solution' can be disposed of down the drain. Both solutions need waste beakers (provided) in which the used pipettes should be placed.*

The appropriate procedures for disposing of solutions at the end of this lab practical are:

____

____

____

We are about to begin the lab practical. Please do not turn the page until directed to do so, but read the directions on the front page. Are they any questions before we begin?

Distribute **Part III** booklets and again remind students not to turn the page until the instruct
Part III contains student instructions and answer sheets for both laboratory problems. There is
table on the second page of the booklet. Allow students enough time to read the brief cover direct

Do not turn to page 2 until directed to do so. When you start to work, be sure to fill out all of t information at the top of the answer sheets. Are they any additional questions?

If there are no further questions, the students should be ready to start **Part III.**

You may begin.

After **one hour and thirty minutes**, give the following directions.

This is the end of the lab practical. Please stop and bring me your answer sheets. Thank you for your cooperation during this portion of the exam.

Collect all the lab materials. Make sure that the student has filled in his or her name and other required information on the answer sheets. At this point, you might wish to take a few minutes to discuss the lab practical with the students. They can learn about possible observations and interpretations and you can acquire feedback as to what they actually did and how they reacted to the problems. After this discussion, please take a few minutes to complete the Post-Exam Questionnaire; this information will be extremely useful to the USNCO subcommittee as they prepare for next year's exam.

Please remember to return the post-exam Questionnaire, the answer sheets form **Part III,** the Scantron sheets from **Part I,** and the 'Blue Books" from **Part II** in the overnight return envelope you were provided to this address:

American Chemical Society
U.S. National Chemistry Olympiad Office
1155 16th Street, NW
Washington, DC 20036

The label on the UPS Express Pak envelope should have this address and your return address already. The cost of the shipping is billed to ACS - USNCO. You can keep copy of the tracking number to allow you to track your shipment.

Wednesday, April 28, 2010, is the ***absolute*** deadline for ***receipt*** of the exam material. Materials received after this deadline **CANNOT** be graded. Be sure to have your envelope sent no later than *Tuesday, April 27, 2010* for it to arrive on time.

THERE WIL BE NO EXCEPTIONS TO THIS DEADLINE DUE TO THE TIGHT SCHEDULE FOR GRADING THIS EXAMINATION.

Lab Problem #1: Materials and Equipment

Each student should have available the following equipment and materials:

Materials

- Three standard size (18 or 20 × 150mm) test tubes
- One 150 or 250 mL beaker to hold the test tubes
- Four 5 mL capacity Beral-style pipets
- Four pieces of waxed weighing paper
- One 100 or 150 mL Erlenmeyer flask with stopper
- One 12-hole white spot plate (porcelain or polyurethane)
- Several wooden stirring sticks, the kind used for stirring coffee
- Access to distilled water, preferably individual bottles at each lab station

Chemicals

- Four capped numbered vials (20–30 mL capacity) containing approximately 3–5 g of each of the following solids: $FeCl_3{\cdot}6H_2O$, $CoSO_4{\cdot}7H_2O$, $CuCl_2{\cdot}2H_2O$, and $K_2C_2O_4{\cdot}H_2O$

Vial	Substance
#1	$FeCl_3{\cdot}6H_2O$
#2	$CoSO_4{\cdot}7H_2O$
#3	$CuCl_2{\cdot}2H_2O$
#4	$K_2C_2O_4{\cdot}H_2O$

Obviously, do not identify or label the contents of each vial!

- 25–30 mL of concentrated ammonia solution per student. To make this solution for a group of 25–30 students, using stock (14.8M) ammonium hydroxide, $NH_4OH(aq)$ mix 250 mL of the ammonium hydroxide with 500 mL water to make a total volume of 750 mL ammonia solution. The 100 or 150 mL flask should be labeled ‘Ammonia Solution’.

Lab Problem #1 Notes

- Be sure that the solids are powdered and dry. In the case of the iron (III) chloride you may want to grind it fine as it has a tendency to clump.
- Students will be warned that the ammonia solution is pungent and to take caution as it is used.

Safety: It is your responsibility to ensure that all students wear safety goggles and gloves during the lab practical. A lab coat or apron for each student is desirable but not mandatory. You will also need to give students explicit directions for handling spills and for disposing of waste materials, following approved safety practices for your examination site. Please check and follow procedures appropriate for your site.

Lab Problem #2: Materials and Equipment

Each student should have available the following equipment and materials:

Materials

- Three small (10 × 75 mm) test tubes
- One 50 mL beaker to hold the test tubes
- One 100 or 150 mL beaker to hold the labeled silver nitrate, seawater, and potassium chromate pipets
- Three 5 mL Beral–style pipet (graduated or ungraduated, thin or regular stem)

Chemicals

- Approximately 30 mL of seawater in a covered 100 or 150 mL flask labeled ‘seawater’
- Two 5 mL capacity Beral-style pipets filled with 5.0×10^{-4} mol $AgNO_3$ per gram solution. To make this solution, dissolve 2.13 g of solid $AgNO_3$ in 25.0 mL DI water. Store in a dark, covered container until ready to apportion to students. Pipets should be labeled ‘$AgNO_3$ solution’. It should be clearly labeled "Caution - Do not get on Skin or Clothes - Will cause Stains"
- One Beral-style pipet containing potassium chromate solution
- The concentration of this solution should be approximately 1M (M_r K_2CrO_4 = 194). This pipet should be labeled ‘K_2CrO_4 solution’. To make this solution, dissolve 0.4 g K_2CrO_4 / 2 mL per student or 10 g in 50 mL for 25 students.
- Neither solution ‘$AgNO_3$ solution’ nor ‘K_2CrO_4 solution’ can be disposed of down the drain. Both solutions need waste beakers in which the used pipettes are placed.

Lab Problem #2 Notes:

- For the ocean water, if you live near the coast, obtain a sample directly from the ocean. Let any solids settle before apportioning to students. If you do not have an available source of ocean water, you may simulate a sample by dissolving 2.80 g of NaCl in 100 mL of distilled water (don’t use tap water as it likely already contains measurable amounts of chloride). You may also use common commercial laboratory seawater preparations that include approximate percentages of minerals found in ocean water.
- Make sure to use DI water in making the silver nitrate solution. Ideally, this solution is made just prior to use the day of the exam.
- The concentration of the potassium chromate solution is not critical but should be approximately 1M.

Safety: It is your responsibility to ensure that all students wear safety goggles and gloves during the lab practical. A lab coat or apron for each student is desirable but not mandatory. You will also need to give students explicit directions for handling spills and for disposing of waste materials, following approved safety practices for your examination site. Please check and follow procedures appropriate for your site.

2010 USNCO Part III Answers

Lab Problem 1

Students were expected to create different complex compounds by combinations of the hydrate compounds provided with the aqueous ammonia solution. Students might have thought also to react the hydrates with an aqueous oxalate solution or to slowly add water to samples of each hydrate. For example, adding H_2O slowly to a small amount of copper(II) chloride in one of the test tubes produces a color change as the dihydrate of this salt forms a tetrahydrate.

Vial	**Compound**
1	Yellow-Orange, $FeCl_3 \cdot 6H_2O$
2	Pinkish, $CoSO_4 \cdot 7H_2O$
3	Green, $CuCl_2 \cdot 2H_2O$
4	White, $K_2C_2O_4 \cdot H_2O$

Compound	**Possible Formula**	**Observation**
$CuCl_2 \cdot 2H_2O + H_2O$	$CuCl_2 \cdot 4H_2O$	green → blue
$CuCl_2 \cdot 2H_2O$ + ammonia solution	$Cu(NH_3)_4$	deep blue color change
$CoSO_4 \cdot 7H_2O$ + ammonia solution	$Co(NH_3)_6$	bright blue-green color change
$FeCl_3 \cdot 6H_2O$ + ammonia solution	$Fe(NH_3)_6$	Brown-purple gelatinous ppt.
$K_2C_2O_{4(aq)} + FeCl_3 \cdot 6H_2O$	$K_3[Fe(C_2O_4)_3]$	greenish color change
$K_2C_2O_{4(aq)} + CuCl_2 \cdot 2H_2O$	$K_2[Cu(C_2O_4)_2]$	greenish color change?

Ammonia replaces water in these hydrated compounds to produce complexes that include NH_3 surrounding the central metal cation. Possible formulas might also include ligand combinations of ammonia, water, and chloride or sulfate as part of the complex.
Possible sketches of these structures show the central Cu, Fe, and Co cations surrounded by the NH_3 ligands in tetrahedral, square planar geometry, or octahedral geometries.

Excellent Results:
Students attempted as many matches as possible, creating a legible and systematically organized table to communicate their results. The nomenclature of the possible complexes was clear and the formulas used the proper coordinate complex compound was accurate. Drawings for the possible structures included three-dimensional representations of the complexes and indicated how and where isomers might also be formed. It was drawn/noted that the oxalate ion was a bidentate and three ions were able to coordinate with the iron (III) cation.

Average Results:
Students attempted to create and draw only the requested five complexes. A listing o combinations and the observed results was provided. At least one possible complex geom was shown.

Below Average Results:
Students created fewer than the requested five complexes. No systematic table or chart was provided to indicate the possible compounds formed. One or no possible geometries were provided. Errors in the nomenclature and formulas were evident.

Lab Problem 2

Sample Data:

Initial mass of the seawater and pipet	3.121 g
Final mass of the seawater and pipet	2.243 g
Initial mass of silver nitrate and pipet	2.820 g
Final mass of silver nitrate and pipet	1.918 g

Sample Student Calculations:
3.121 g – 2.243 g = 0.878 g seawater used
2.820 g – 1.918 g = 0.902 g silver nitration solution used
Molar masses: NaCl = 58.44 g/mol
$AgNO_3$ = 169.87 g/mol

0.902 g $AgNO_3$ x 5.0 x 10^{-4} mol/g $AgNO_3$ = 4.51 x 10^{4} mole $AgNO_3$

4.51 x 10^{4} mole $AgNO_3$ = mole Ag^{+} ; mole Cl^{-}

4.51 x 10^{4} mole Cl^{-} x 35.5 g/mol Cl^{-} = 1.60 x 10^{-2} g Cl^{-}

1.60 x 10^{-2} g Cl^{-}/0.878 g seawater x 100 = 1.82% Cl^{-} in solution by mass
(A value of 1.80-1.90% is generally accepted)

Excellent Results:
At least two trials were attempted using both of the filled $AgNO_3$ pipets and averaging results. These titrations were completed in the small test tubes provided. A clear and organized table showed the initial and final masses of both the seawater and silver nitrate pipets. Observations of the silver chloride and the silver chromate formation were noted. Calculations were legible, organized, and followed a logical sequence in order to determine the mass of chloride ion

present and the final mass percentage present. Use of the K_{sp} values was made to ow the AgCl then Ag_2CrO_4 selective order of precipitation. Assumptions included the precipitation of AgCl from solution, the equivalent molar ratio of Ag^+: Cl^-, the presen drop or two of the chromate solution to the seawater to be sufficient to create a white/red c change endpoint. Error included the subjective judgment of the endpoint to distinguish th complete precipitation of the chloride from the beginning of the precipitation of the chromate, and the additional drop or two overshooting of the endpoint to turn the solution entirely reddish.

Average Results:
Only one trial was attempted. Leftover materials were not utilized to complete additional experiments. Observations were made to determine the endpoint. Calculations show a logical sequence to solve this problem, but may not have been clearly organized. Only one point was included for the assumptions and error.

Below Average Results:
Not all of the materials were used. Calculations did not show evidence of logical sequence in problem solving. Observations were incomplete. One or no points were made regarding error or assumptions.