2023 U.S. NATIONAL CHEMISTRY OLYMPIAD

NATIONAL EXAM PART III

Prepared by the American Chemical Society Chemistry Olympiad Examinations Task Force

OLYMPIAD LABORATORY PRACTICAL TASK FORCE

Kelli Slunt, **Chair**, *University of Mary Washington*, Fredericksburg, VA

Jesse Bernstein, *Miami Country Day School*, Miami FL (retired)
Myra Halpin, *NC School of Science & Mathematics*, Durham, NC (retired)
Iaroslavna Kovalenko, *University of Mary Washington*, Fredericksburg, VA

DIRECTIONS TO THE EXAMINER

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 three parts to the National Olympiad Examination. You have the option of administering the three parts in any order, and you are free to schedule rest breaks between parts.

Part I	**60 questions**	**single-answer multiple-choice**	**1 hour, 30 minutes**
Part II	**8 questions**	**problem-solving, explanations**	**1 hour, 45 minutes**
Part III	**2 lab questions**	**laboratory practical**	**1 hour, 30 minutes**

There are two laboratory tasks to be completed during the 90 minutes allotted to this part of the test. Students may carry out the two tasks in any order they wish and move directly from one to the other within the allotted time. Each procedure must be approved for safety by the examiner before the student begins that procedure.

A periodic table and other useful information are provided on page two for student reference.

Students should be permitted to use non-programmable calculators. The use of a programmable calculator, cell phone, watch, or any other device that can access the internet or make copies or photographs during the exam is grounds for disqualification.

<u>**Students are permitted to request one replacement or refill of a chemical during the laboratory period. Please indicate on the exam sheet the item replaced or refilled.**</u>

DIRECTIONS TO THE EXAMINEE - 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 examination site.

Do not forget to turn in your U.S. citizenship/Green Card Holder statement before leaving the testing site today.

STUDENT USNCO ID:

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

CONSTANTS

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$R = 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$

$F = 96{,}500 \text{ C mol}^{-1}$

$F = 96{,}500 \text{ J V}^{-1} \text{ mol}^{-1}$

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

$h = 6.626 \times 10^{-34} \text{ J s}$

$c = 2.998 \times 10^{8} \text{ m s}^{-1}$

0 °C = 273.15 K

1 atm = 1.013 bar = 760 mm Hg

Specific heat capacity of H_2O = $4.184 \text{ J g}^{-1} \text{ K}^{-1}$

EQUATIONS

$$E = E^{\circ} - \frac{RT}{nF}\ln Q$$

$$\ln K = \left(\frac{-\Delta H^{\circ}}{R}\right)\left(\frac{1}{T}\right) + \text{constant}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

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** 78.97	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** 95.95	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** (263)	107 **Bh** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Ds** (281)	111 **Rg** (272)	112 **Cn** (285)	113 **Nh** (286)	114 **Fl** (289)	115 **Mc** (289)	116 **Lv** (293)	117 **Ts** (294)	118 **Og** (294)

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)**

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.

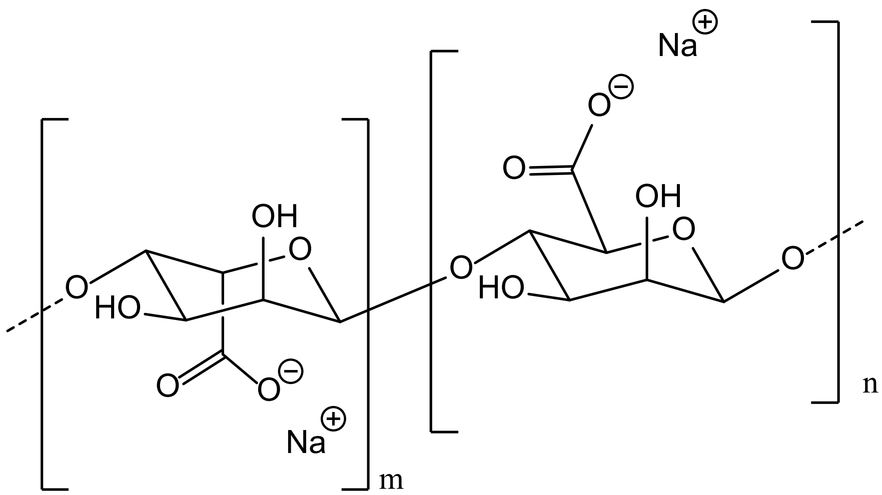
Safety Considerations
You are required to wear approved eye protection at all times during this laboratory practical. You also must follow all directions given by your examiner for dealing with spills and with disposal of wastes.

Lab Problem 1

Question: Using the provided materials, determine the molar mass and pKa of an unknown monoprotic weak acid.

Lab Problem 2

Question: Sodium alginate is isolated from seaweed and is used in molecular gastronomy.



In the presence of certain cations, the polymer can create cross-links and gel spheres are formed. You will be provided with a solution of sodium alginate and three solutions each containing one of the following compounds; calcium chloride, magnesium chloride or potassium chloride. Determine which cation produces the strongest cross-links in the polymer to form hydrogel spheres.

Safety: do not taste or consume the produced liquid spheres

STUDENT USNCO ID:

Answer Sheet for Laboratory Practical **Problem 1**

Examinor's Name: ____

ACS Local Section Name: ____

1. Give a brief description of your experimental plan.

2. Record your data/observations.

For safety reasons, before beginning your experiment you must get approval from the examiner.

Examiner’s Initials:

STUDENT USNCO ID:

3. Show all calculations.

4. The molar mass of the unknown weak acid is ____ g/mol. The pKa of the weak acid is _______.

Proctor, please indicate the item replaced or refilled provided (if any):

STUDENT USNCO ID:

Answer Sheet for Laboratory Practical **Problem 2**

Examinor's Name:____

ACS Local Section Name:____

1. Give a brief description of your experimental plan.

2. Record your data/observations.

For safety reasons, before beginning your experiment you must get approval from the examiner.

Examiner's Initials:

STUDENT USNCO ID:

3. The cation that creates the strongest cross-links in the alginate polymer is ….

4. Based on the structures of the polymer and cations, briefly explain your experimental observations and the observed differences in cross-linking/spherification.

Proctor, please indicate the item replaced or refilled provided (if any):

2023 U.S. NATIONAL CHEMISTRY OLYMPIAD

NATIONAL EXAM PART III
EXAMINER'S INSTRUCTIONS

Prepared by the American Chemical Society Chemistry Olympiad Examinations Task Force

OLYMPIAD LABORATORY PRACTICAL TASK FORCE

Kelli Slunt, **Chair**, *University of Mary Washington*, Fredericksburg, VA

Jesse Bernstein, *Miami Country Day School*, Miami FL (retired)
Myra Halpin, *NC School of Science & Mathematics*, Durham, NC (retired)
Iaroslavna Kovalenko, *University of Mary Washington*, Fredericksburg, VA

Thank you for administering the 2023 USNCO laboratory practical on behalf of your Local Section. It is essential that you follow the instructions provided in order to ensure 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 and the materials separated for Lab Problem #1 and for Lab Problem #2.

Students are permitted to request one replacement or refill of a chemical during the laboratory period. Please indicate on the exam sheet the item replaced or refilled.

It is your responsibility to ensure that all students wear approved eye protection at all times, tie back long hair into a ponytail, and wear close-toed shoes during this laboratory 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.

After the students have settled, read the following *instructions* 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 safety goggles at all times.*** *Please wash off any chemicals spilled on your skin or clothing with large amounts of tap water.*

(Continued on the next page)

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. 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 instruction is given. Part III contains student instructions and answer sheets for both laboratory problems. There is a periodic table on page two of the booklet. Allow students enough time to read the brief cover directions.

Do not turn to page three until directed to do so. When you start to work, be sure to fill out all of the 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 their 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 that was sent by e-mail through Formsite; this information will be extremely useful to the USNCO subcommittee as they prepare for next year's exam.

Please remember to return the answer sheets from Part III, the Scantron® sheets from Part I, and the Part II booklets in the UPS Next Day return envelope you were provided to this address:

American Chemical Society
U.S. National Chemistry Olympiad
1155 16th Street, NW – Room 834
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 a copy of the tracking number to allow you to track your shipment.

Wednesday, April 26, 2023, 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 **Monday, April 24, 2023** for it to arrive on time.

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

NOTE THAT THE EXAMINER WILL NEED TO INITIAL EACH STUDENT'S EXPERIMENTAL PLAN. PLEASE DO NOT COMMENT ON THE PLAN OTHER THAN LOOKING FOR ANY POTENTIAL UNSAFE PRACTICES.

(Continued on the next page)

Each student should have available the following:

<u>Materials needed:</u>

Each student should have available the following equipment and materials:

- One (1) graduated cylinder, 10 mL
- Six (6) Beral pipets – these do not need to be graduated but can have graduations – two could be prefilled with the indicator solutions or solutions could be provided in vials and empty pipets
- Three (3) glass or plastic stirring rods
- Six (6) beakers, 50 or 100 mL
- Three (3) pieces of wax paper or glassine weigh paper
- One (1) spatula
- One (1) watch glass or petri dish
- One (1) plastic or ceramic well plate
- One (1) ruler
- One (1) plastic spoon
- Access to balance that can measure to nearest 0.01 g. If one balance per student is not available, 2 to3 students could share a balance.
- One (1) wash bottle filled with distilled or deionized water, at least 500 mL, labelled appropriately
- Access to paper towels and a sink with running water

<u>Chemicals needed:</u>

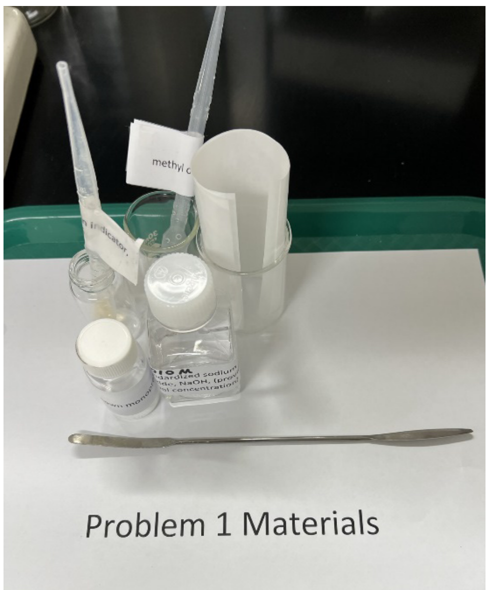
Sample labels for containers are provided.

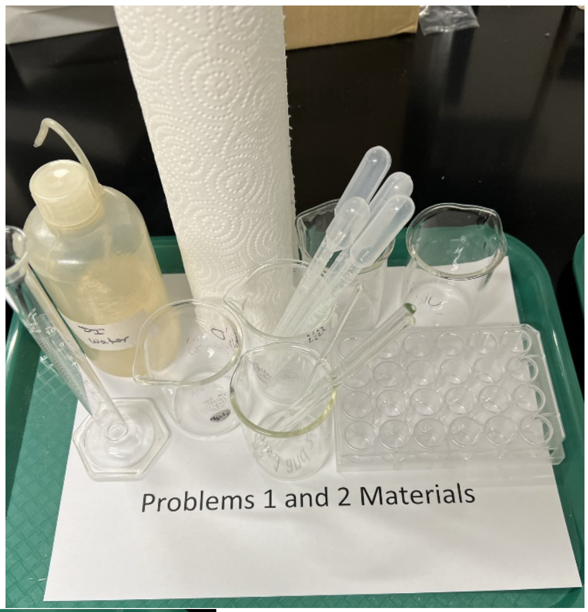
- Solid benzoic acid **(labelled as unknown monoprotic acid)**
  - 0.5 g per student
- Standardized NaOH, 1 M reported to three significant figures
  - 20 mL per student
- Phenolphthalein indicator
  - 1.0 mL in a labelled Beral pipet or vial with dropper available
  - Dissolve 0.1 g phenolphthalein in 80 mL of 95% ethanol and add sufficient water to make 100 mL solution
- Methyl orange indicator
  - 1.0 mL in a labelled Beral pipet or vial with dropper available
  - Dissolve 0.1 g of methyl orange in 80 mL of 95% ethanol and add sufficient water to make 100 mL solution
- Sodium alginate solution, 2% (w/v)
  - **Must be prepared at least one day in advance and stored in refrigerator until used by students.**
  - 10 mL per student
  - Dissolve 2 g of sodium alginate into 100 mL of water(must be devoid of any calcium – deionized or distilled water). Mix the solution in a blender or mixer to thoroughly disperse the polymer in the solution. Mixture should be smooth and allowed to sit at least overnight to reduce foaming. Color the solution with food coloring (any color is fine).
- Magnesium chloride, 2 M
  - 30 mL per student
  - Dissolve 406 g of magnesium chloride hexahydrate in enough water to make 1 L of solution
- Calcium chloride, 2 M
  - 30 mL per student
  - Dissolve 294 g of calcium chloride dihydrate in enough water to make 1 L of solution
- Potassium chloride, 2 M – 30 mL per student
  - Dissolve 150.8 g of potassium chloride in enough water to make 1 L of solution

Standardization instructions for NaOH:

1. Dissolve 40 grams of solid NaOH in enough distilled or deionized water to create one liter solution.
2. Weigh out approximately 0.8 grams of potassium hydrogen phthalate (KHP, molecular weight 204.23g/mol) to at least 3 decimal places and dissolve in 50-75 mL of water in an Erlenmeyer flask. Recordthe amount of KHP used.
3. Add 2-3 drops of phenolphthalein indicator to the KHP solution.
4. Titrate the solution with prepared NaOH solution until a faint pink endpoint. Record volume of NaOHsolution used in the titration.
5. Repeat.
6. Convert grams of KHP to mol NaOH noting a 1:1 mole ratio of KHP to NaOH.
7. Divide moles of NaOH by the volume of NaOH used to determine molarity.
8. Report the average molarity on the labels for the students.

<u>Suggested Set-up Photos</u>





2023 UNITED STATES NATIONAL CHEMISTRY OLYMPIAD
National Exam Part III Rubric

Lab Problem 1 Prompt:
Using the provided materials, determine the molar mass and pKa of an unknown monoprotic weak acid.

Equipment and materials provided:
Please see attached instructions for site coordinators.

Questions for the Examination Paper:

1. Give a brief description of your experimental plan.
2. Record your data/observations.
3. Show all calculations.
4. The molar mass of the unknown weak acid is ____ M. The pK_a of the weak acid is _______.

Suggested Experimental Plan and Expected Results:

Students need to provide an indication of number of drops in a milliliter.

Starting with a known mass of the unknown weak acid, determine the molar mass of the weak acid by an acid-base titration. One will note how many drops of known concentration of base it takes to reach a phenolphthalein end point. Using the volume of base and known concentration, determine the moles of NaOH used to reach the end point. As the acid is monoprotic, the moles of base equal the moles of acid. Using the moles of acid and mass of weak acid used, determine the molar mass of the unknown acid.

To determine the pK_a, an experiment should be conducted to reach the half equivalence point. After determining the number of drops of NaOH it takes to reach a phenolphthalein end point, perform a titration with the same volume of acid and half the number of drops of base. Approximate the pH of this solution using the provided indicators.

Sample data from Fall 2022 UMW Undergraduate Research Student Iaroslavna Kovalenko

Trial Number	Trial 1	Trial 2	Trial 3	Average
Drops of NaOH, drops	18 drops	15 drops	16 drops	16.3 drops
Volume of NaOH, L	0.00090 L	0.00075 L	0.00080 L	0.00082 L
Mole of NaOH, mol	0.00095 mol	0.00080 mol	0.00085 mol	0.00087 mol
Mass of unknown acid, g	0.10 g	0.10 g	0.10 g	0.10 g

Mole of unknown acid, mol	0.00095 mol	0.00080 mol	0.00085 mol	0.00087 mol
Molar mass of unknown acid, g/mol	105 g/mol	126 g/mol	118 g/mol	116 g/mol

The pKa portion was a little more challenging.

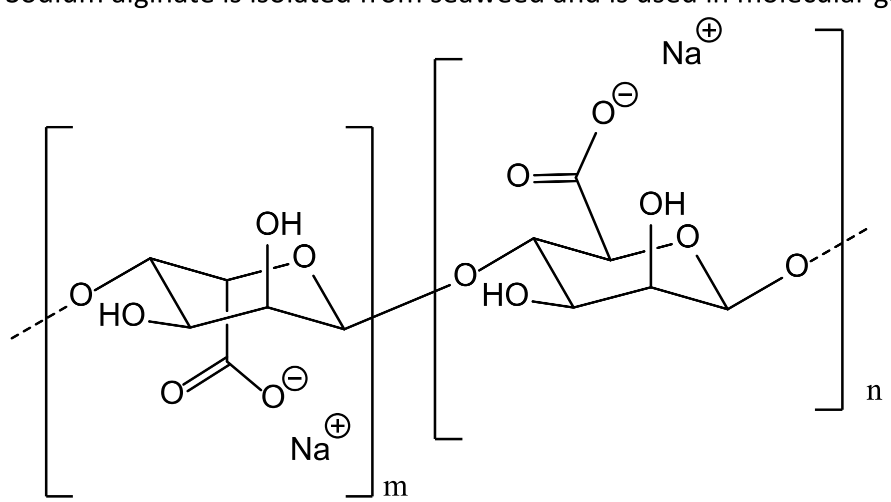
Color of solution after adding 8 drops of NaOH to the acid:

Indicator	**Color of solution**
Phenolphalein	Colorless
Methyl orange	Yellowish orange

Based on these observations, one could approximate the pKa in the color change region of methyl orange or bromocresol green – around pKa of 4.

Alternatively, students could titrate the unknown acid with the different indicators and note the color and the midway point of the titration.

<u>Lab Problem 2 Prompt:</u>
Sodium alginate is isolated from seaweed and is used in molecular gastronomy.



In the presence of certain cations, the polymer can create cross-links and gel spheres are formed. You will be provided with a solution of sodium alginate and three solutions each containing one of the following compounds; calcium chloride, magnesium chloride or potassium chloride. Determine which cation produces the strongest cross-links in the polymer to form hydrogel spheres.

Safety: do not taste or consume the produced liquid spheres.

Equipment and materials provided:
Please see attached instructions for site coordinators.

Questions for the Examination Paper:

1. Give a brief description of your experimental plan.
2. Record your data/observations.
3. The cation that creates the strongest cross-links in the alginate polymer is ….
4. Based on the structures of the polymer and cations, briefly explain your experimental observations and the observed differences in cross-linking/spherification.

Suggested Experimental Plan and Expected Results:

Students should plan to drop sodium alginate solution into different solutions of cations. The best plan would be to create dilution series of cations at varying concentrations and determine the minimum concentration for spherification. Students could also dilute the sodium alginate to determine the minimum concentration for spherification.

Results from UMW Student Undergraduate Research Student Iaroslavna Kovalenko

Cation	**Results**
Calcium	Well formed spheres occur at concentrations as low as 0.1 M. Spheres formed in concentration of calcium between 0.09 and 0.04 M were softer and could be easily disrupted. Spheres did not form at concentrations lower than 0.04 M. <u>Varying concentrations of sodium alginate dropped into 2 M calcium chloride solution</u>: Spheres with concentration 1-2% sodium alginate were strong and elastic, whereas spheres formed from 0.1-0.9% sodium alginate were soft and could break easily.
Magnesium	Under varying concentrations of magnesium and sodium alginate, spheres do not form. Rather, sheets or films were observed in the solutions.
Potassium	Spheres do not form with the concentrations of solutions formed.