CHIMIESOLYMPIAD
LËTZEBUERG 2022

SEMI-FINALS: Problems

Dear students,

We congratulate you for your participation in the Chemistry Olympiad and we wish you lots of success in this second round as well as in your studies and in all of your future endeavours. We also congratulate you for having succeeded in the first round, which has enabled you to tackle the "Problems" round today. **Before undertaking this next round, please carefully read the following instructions.**

Attached you will find 4 questions. The subjects of these questions are: general chemistry, stoichiometry, pH, redox and organic chemistry.

You have **two hours** to answer these questions. You can use a non-programmable calculator, but you cannot have any personal documents on you.

Include your name and your institution's name at the start of **each** question. Write your answers to each of the questions on the question paper (front and back, if necessary). **Clearly indicate your reasoning and your calculations. Justify your answers and indicate the units in the final answers.** The last page is a draft sheet which will not be taken into account for the final assessment. Detach the two first pages and keep them for reference.

Following the results of this second round, the 12 best students will be invited to participate in a final (practical) round, which will take place on **Saturday, April 30th 2022, at the University of Luxembourg's Limpertsberg laboratories**. This final round will determine the 4 laureates of the national Chemistry Olympiad, and will also constitute the Luxembourg team for the 54th IChO, which will be organized by China, from July 10th to July 20th 2022. For more information, please see https://chimie.olympiades.lu/.

The results of this second round will be taken into account for the ranking of the four finalists !!!

Best wishes and good luck.
The Chemistry Olympiad organisers

Detach this sheet and keep it for information.

LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Éducation nationale,
de l'Enfance et de la Jeunesse
ACLg
UNIVERSITÉ DU LUXEMBOURG
Fonds National de la Recherche Luxembourg
CHAMBRE DE COMMERCE LUXEMBOURG
CHAMBRE DES SALARIES LUXEMBOURG
andré losch fondatioun

Useful Constants

(Detach this page if necessary)

relative atomic mass — A_r
element — X
atomic number — Z

1 I a	2 II a		3 III b	4 IVb	5 V b	6 VI b	7 VII b	8 VIII b	9	10	11 I b	12 II b	13 III a	14 IV a	15 V a	16 VI a	17 VII a	18 VIII a
1,01 H 1																		4,00 He 2
6,94 Li 3	9,01 Be 4												10,81 B 5	12,01 C 6	14,01 N 7	16,00 O 8	19,00 F 9	20,18 Ne 10
22,99 Na 11	24,31 Mg 12												26,98 Al 13	28,09 Si 14	30,97 P 15	32,07 S 16	35,45 Cl 17	39,95 Ar 18
39,10 K 19	40,08 Ca 20		44,96 Sc 21	47,88 Ti 22	50,94 V 23	52,00 Cr 24	54,94 Mn 25	55,85 Fe 26	58,93 Co 27	58,69 Ni 28	63,55 Cu 29	65,39 Zn 30	69,72 Ga 31	72,61 Ge 32	74,92 As 33	78,96 Se 34	79,90 Br 35	83,80 Kr 36
85,47 Rb 37	87,62 Sr 38		88,91 Y 39	91,22 Zr 40	92,91 Nb 41	95,94 Mo 42	Tc* 43	101,07 Ru 44	102,91 Rh 45	106,42 Pd 46	107,87 Ag 47	112,41 Cd 48	114,82 In 49	118,71 Sn 50	121,75 Sb 51	127,60 Te 52	126,90 I 53	131,29 Xe 54
132,91 Cs 55	137,33 Ba 56	(1) 57 - 70	174,97 Lu 71	178,49 Hf 72	180,95 Ta 73	183,9 W 74	186,21 Re 75	190,21 Os 76	192,22 Ir 77	195,08 Pt 78	196,97 Au 79	200,59 Hg 80	204,38 Tl 81	207,21 Pb 82	208,98 Bi 83	Po* 84	At* 85	Rn* 86
Fr* 87	Ra* 88	(2) 89 - 102	Lr* 103	Rf* 104	Db* 105	Sg* 106	Bh* 107	Hs* 108	Mt* 109	Ds* 110	Rg* 111	Cn* 112	Nh* 113	Fl* 114	Mc* 115	Lv* 116	Ts* 117	Og* 118

1) Lanthanides	138,92 La 57	140,12 Ce 58	140,91 Pr 59	144,24 Nd 60	Pm* 61	150,36 Sm 62	151,97 Eu 63	157,25 Gd 64	158,93 Tb 65	162,50 Dy 66	164,93 Ho 67	167,26 Er 68	168,93 Tm 69	173,04 Yb 70
2) Actinides	Ac* 89	232,04 Th 90	231,04 Pa 91	238,03 U 92	Np* 93	Pu* 94	Am* 95	Cm* 96	Bk* 97	Cf* 98	Es* 99	Fm* 100	Md* 101	No* 102

Constants

$R = 8{,}31\ J\cdot mol^{-1}\cdot K^{-1}$ $\quad$ $1\ F = 9{,}65\cdot 10^{4}\ C\cdot mol^{-1}$

$R = 8{,}21\cdot 10^{-2}\ L\cdot atm\cdot mol^{-1}\cdot K^{-1}$ $\quad$ $N_A = 6{,}022\cdot 10^{23}\ mol^{-1}$

Volume of an ideal gas mole at 273 K and 101 325 Pa : 22,4 $dm^3\cdot mol^{-1}$ ($L\cdot mol^{-1}$)

Simplified pH formulas:

Strong acid	Weak acid	Strong base	Weak base
$pH = -\log c_{acid}$	$pH = \frac{1}{2}(pK_a - \log c_{acid})$	$pH = 14 + \log c_{base}$	$pH = 14 - \frac{1}{2}(pK_B - \log c_{base})$

Buffer mix: $pH = pK_a + \log\frac{c_{base}}{c_{acid}}$ $\qquad$ at 25 °C : $K_w = K_{H_2O} = [H_3O^+]\cdot[OH^-] = 1{,}0\cdot 10^{-14}$

Thermochemistry:

$\Delta_R H = Q_p + W$	$\Delta_R G = \Delta_R H - T\cdot\Delta_R S$
$\Delta_R S = \frac{Q}{T}$	$\Delta_R G = -R\cdot T\cdot \ln K$

LE GOUVERNEMENT DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Éducation nationale, de l'Enfance et de la Jeunesse
ACLg
uni.lu UNIVERSITÉ DU LUXEMBOURG
Fonds National de la Recherche Luxembourg
CHAMBRE DE COMMERCE LUXEMBOURG
CHAMBRE DES SALARIES LUXEMBOURG
andré losch fondatioun

NAME : ______________________________________

Given name : ___________________________________

School : _______________________________________

Problem I: Compounds of phosphorus

1a	1b	1c	1d	1e	1f	1g	Total Problem I
1	2	3	5	3	1	3	18

Phosphoric acid is commonly used in organic or inorganic chemistry, but also in the food industry. It is found in all cola soft drinks.

As phosphoric acid is a triacid, the acidity constants are as follows:

$$pK_{a_1} = 2{,}16;\ \ pK_{a_2} = 7{,}21;\ \ pK_{a_3} = 12{,}3;$$

a) Establish the equation for the first protolysis of phosphoric acid.

b) Calculate the pH of a 0.050 M solution of H_3PO_4.

c) Calculate the pH of a solution A containing 13.61g KH_2PO_4 and 17.42g K_2HPO_4 in 100 mL solution.

d) Calculate the volume of 0.5 M HCl that must be added to solution **A** to obtain a solution with a pH = 7.12.

The element phosphorus is the source of many inorganic compounds, which have very different geometrical structures.

e) Indicate the spatial structure of the compounds below.

P_4	PCl_3	PCl_5

In the gas phase, phosphorus pentachloride decomposes into phosphorus trichloride and chlorine. This is a chemical equilibrium, and the equilibrium constant is K = 3.25.

For a mole of PCl_5 : $\Delta_R H_T^0 = 72{,}2$ kJ and $\Delta_R S_T^0 = 143$ J/K

f) Draw up the equation for the decomposition of phosphorus pentachloride and indicate the aggregate states by subscripts.

g) Determine by calculation the temperature T at which decomposition takes place spontaneously.

NAME : ______________________________________

Given name : __________________________________

School : _______________________________________

Problem II : polonium

2a	2b	2c	2d	2e	2f	2g	Total Problem II
2	1	3	5	4	1	5	21

Polonium is a radioactive element in group VI, that was discovered in 1898 by Marie Curie. It's a very rare element that occurs in traces in several minerals, but nowadays, it's mostly produced by bombarding ${}^{209}_{83}\text{Bi}$ with neutrons. This first leads to the production of ${}^{210}_{83}\text{Bi}$, which has a short half-life and decays by emission of a beta minus particle (an electron):

$$ {}^{209}_{83}\text{Bi} + {}^{1}_{0}\text{n} \rightarrow {}^{210}_{83}\text{Bi} + \gamma $$

$$ {}^{210}_{83}\text{Bi} \rightarrow {}^{210}_{84}\text{Po} + {}^{0}_{-1}\beta $$

Polonium-210 has a half-life of 138 days and decays by emission of an alpha particle (He^{2+}).

a) Give the electron configuration of polonium.

b) Indicate which nuclide is formed by decay of polonium-210.

Because of its short half-life and the intense alpha radiation, metallic polonium and its compounds spontaneously heat up; a one-gram sample of polonium produces 141 W. That's why it is used to provide heat in radioisotope heater units (RHU), in a satellite for instance, and also to convert the heat released by the decay into electricity in radioisotope thermal generators (RTG).

Plutonium-238 has recently been used rather than polonium. ${}^{238}\text{Pu}$ has a very longer half-life but provides less energy (0,56 $\text{W}\cdot\text{g}^{-1}$).

c) Calculate the power (in $\text{W}\cdot\text{g}^{-1}$) of polonium-210 after one year.

d) After 5 years, the remaining power of ^{238}Pu is about 96% of its initial value. Estimate the half-life of plutonium-238.

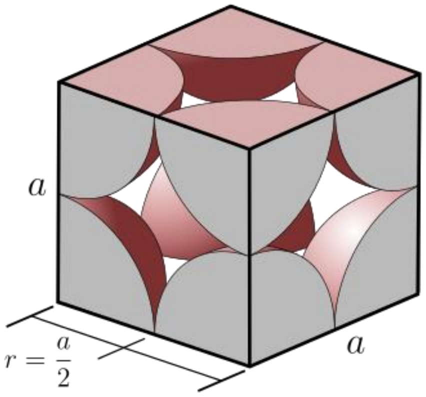
The activity A of a radioactive source corresponds to its decay rate. Activity can be expressed in Bq (Becquerel, 1 Bq corresponds to 1 decay per second) or in Ci (Curie, 1 Ci = $3{,}7 \cdot 10^{10}$ Bq). The activity A of a radioactive source at the time t is given by the relation :

$$A(t) = \lambda \cdot N(t)$$

λ is the decay constant given by : $\lambda = \frac{\ln 2}{t_{1/2}}$ and $N(t)$ is the number of radioactive atoms remaining at the time t.

e) Calculate the activity of 1 mg of Polonium-210 in Ci.

Polonium is the only known element having a simple cubic structure, with atoms at each corner of the cube:



f) Determine the number of polonium atoms inside the unit cell :

g) Calculate the atomic radius of polonium-210 in picometers, knowing its density $\rho = 9{,}142\ g\cdot cm^{-3}$.

NAME : ______________________________

Given name : ______________________________

School : ______________________________

Problem III: IR spectroscopy and ascorbic acid

3a	3b	3c	3c	Total Problem III
5	2	2	10	19

The principle of infrared (IR) spectroscopy is based on the absorption of light by most molecules in the infrared region of the electromagnetic spectrum and converting this absorption into molecular vibration. This absorption corresponds specifically to the bonds present in the molecule. With a spectrometer, this absorption of infrared radiation by the sample material is measured as a function of wavelength in the form of wavenumbers, typically from 4000 to 600 cm^{-1}. The wavenumber corresponds to the number of wavelengths there are in 1cm. Thus, if $\lambda = 5$ micrometers, the wavenumber is 1/0.0005 cm = 2000 cm^{-1}.

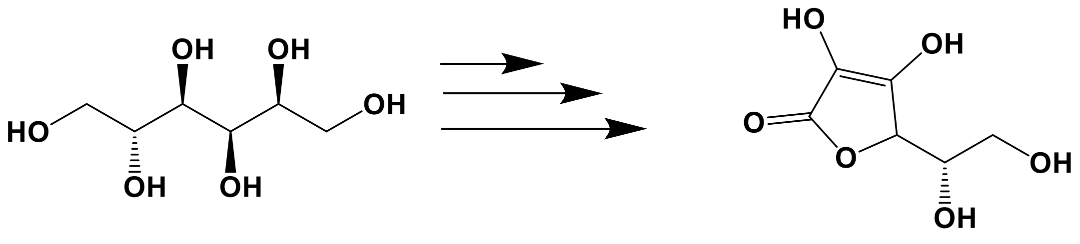
An IR spectrum represents the percentage of infrared light that passes through a sample of an organic substance, depending on the wavenumber of the IR light used. This percentage is, in general, close to the maximum of 100% except when the radiation is absorbed by a functional group. This causes an absorption peak in the spectrum.

The following table gives the wavenumbers of the bands, where certain chemical bonds absorb IR.

Bond type	Wavenumber (cm^{-1})	Absorption band characteristic
O-H alcohol	3200 - 3700	strong, broad
O-H carboxylic acid	2500 - 3200	medium to strong, broad
C-H	2800 - 3100	medium to strong
C=O	1650 - 1740	strong

Industrial synthesis of ascorbic acid

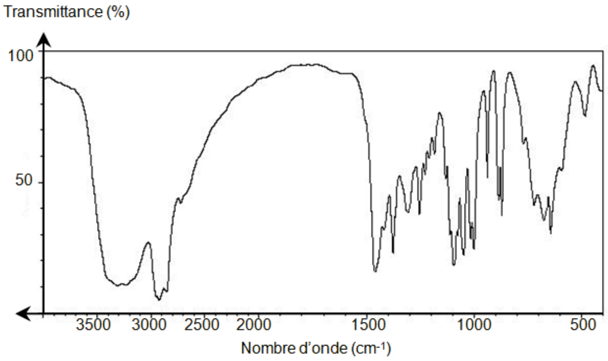
Ascorbic acid (M = 176 $g\cdot mol^{-1}$), or vitamin C, is essential for humans and many animal species. Its dietary deficiency causes painful gingival and joint swellings, bone lesions and hemorrhages, all of which constitute scurvy. It is industrially synthesized from sorbitol. The synthesis according to the Reichstein process takes place in several steps; a simplified reaction scheme is described below.



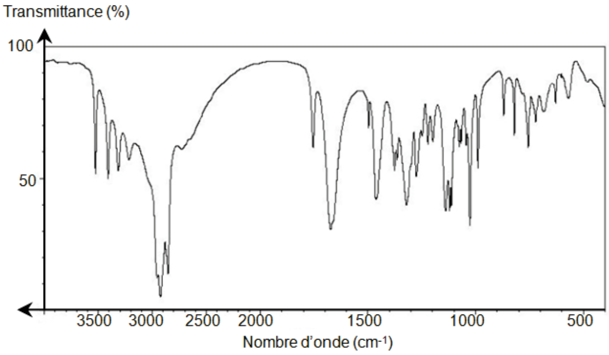
sorbitol

ascorbic acid

a) The progress of the synthesis can be monitored by infrared spectroscopy. Assign the spectra A and B given below to D-sorbitol and ascorbic acid. Justify.

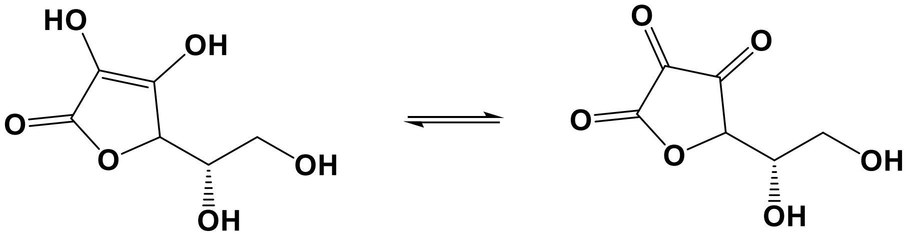


spectrum A



spectrum B

Ascorbic acid is a diprotic acid ($pK_{a_1} = 4{,}2$ and $pK_{a_2} = 11{,}6$) but is also the reductant of the redox couple $C_6H_6O_6$ / $C_6H_8O_6$ (0,166 V).



A 3.0 g vitamin tablet contains, among other things, ascorbic acid. To determine the content of vitamin C, the tablet is completely dissolved in a small amount of distilled water. The mixture is poured quantitatively into a 100.0 mL volumetric flask. 10.0 mL of this solution is retrieved with a pipet. 20.0 mL of an iodine solution of concentration 0.1 mol/L is added (it is assumed that only ascorbic acid reacts with iodine).

The excess of iodine is titrated with a sodium thiosulphate solution of concentration 0.1 mol/L in the presence of a few drops of starch. The endpoint is reached when the blue color disappears. The volume of thiosulphate added at the endpoint is 12.9 mL.

I_2 / I^- : 0,53 V $S_4O_6^{2-} / S_2O_3^{\ 2-}$: 0,09 V

b) Write the equation for the redox reaction between ascorbic acid and iodine.

c) Write the equation for the redox reaction between iodine and thiosulphate.

d) Calculate the content (percentage by mass, %) of ascorbic acid in the tablet.

NAME : ______________________________

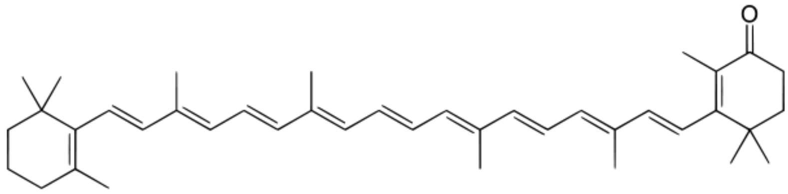
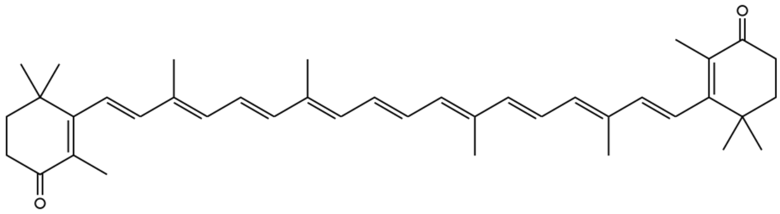
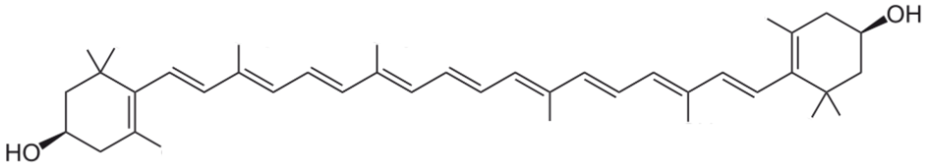
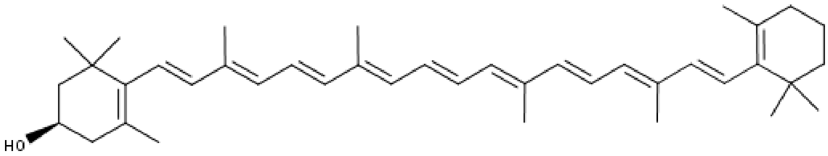
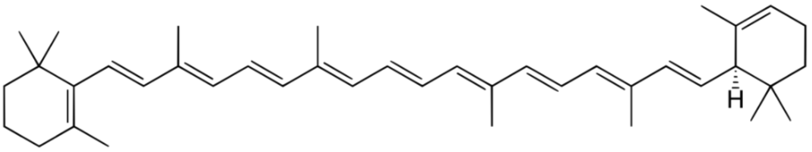
Given name : ______________________________

School : ______________________________

Problem IV: Structure of organic compounds

4a	4b	4c	Total Problem IV
5	11	6	22

Carotenoids are fat-soluble pigments ranging from yellow to red, naturally present in certain foods such as carrots, corn, chanterelles, and salmon. The consumption of foods rich in carotenoids is recommended, as carotenoids are provitamins A, i.e. molecules metabolised by the human body into vitamin A, also known as retinol. Retinol is involved in bone growth and is also an antioxidant that reduces the risk of cancer.

Carotenoids	**Molar mass (g/mol)**	**$\varepsilon_{i,444}$ (L.mol^{-1}.cm^{-1})**
Echinenone	550,86	2158
		
Canthaxanthin	562,84	2200
		
Zeaxanthin	568,89	2348
		
β-Cryptoxanthin	552,85	2386
		
α-Carotene	536,87	2805
		

There are various analytical methods for characterising carotenoids. Three methods are presented below. Using the table above, identify the carotenoids studied in the following statements.

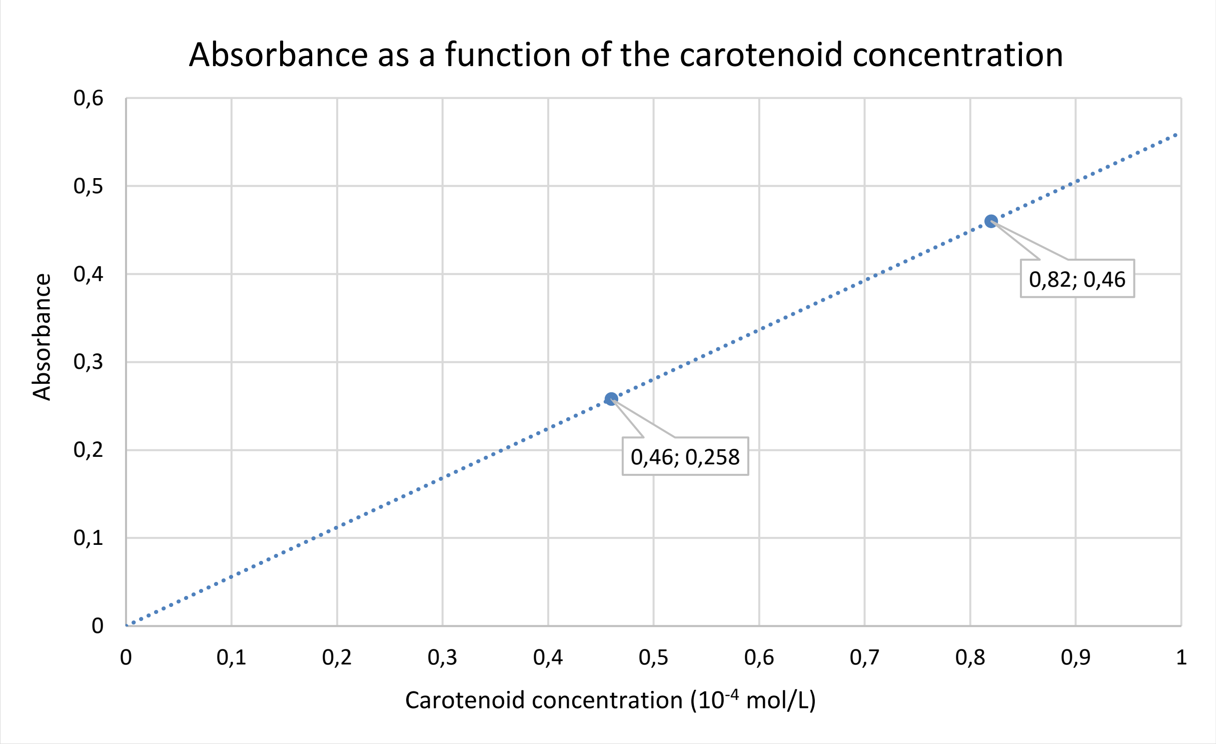
The absorbance, noted A, is the capacity of a solution to absorb a light beam at a specific wavelength. The absorbance depends on 3 parameters: the extinction coefficient ($\varepsilon_{i,\lambda}$, a quantity intrinsic to the substance studied for a given wavelength), the length of the laser's optical path through the solution (L) and the concentration of the substance in solution ([i]).

$$A = \varepsilon_{i,\lambda} \cdot L \cdot [i]$$

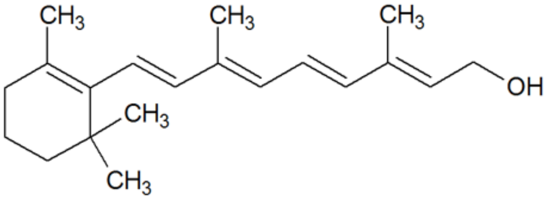
It is therefore possible to determine the concentration of a substance by measuring its absorbance at a specific wavelength. However, this requires knowledge of the extinction coefficient of the sample at the given wavelength, which is not trivial.

An alternative way to calculate the concentration of the sample is to use a calibration line, i.e. to measure the absorbance of solutions with known concentrations of the analysed carotenoid. Then, by performing the absorbance measurement on the sample of unknown concentration and inserting it into the equation of the calibration line, it is possible to deduce the concentration.

a) Knowing that the absorbance measured for a 2.0 cm light path within the sample is 0.316 at a wavelength of 444 nm, and using the graph below, determine which carotenoid is present in the pumpkin. Explain your reasoning using calculations.



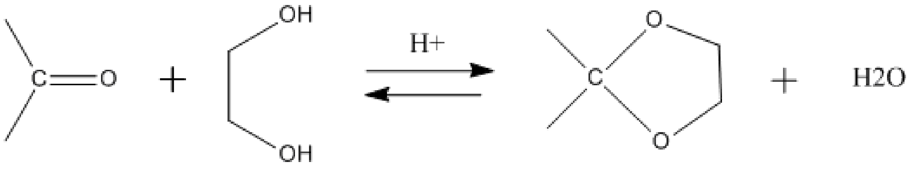
The metabolism of carotenoids produces 2 equivalents of vitamin A. The vitamin A molecule, also called retinol, has an acidic proton that can be titrated with a base. To do this, 50.0 mL of a solution A containing retinol are taken and diluted in an Erlenmeyer flask containing 100.0 mL of deionised water and phenolphthalein as a colour indicator. On gradual addition of NaOH, the phenolphthalein colour change is observed after addition of 48.2 mL. This NaOH solution was previously calibrated by weighing 278.1 mg of oxalic acid ($H_2C_2O_4$) (diprotic acid), which gave a colour change after addition of 47.8 mL of NaOH solution.



(retinol)

b) Knowing that the retinol content in solution A is the result of the metabolism of 1.773 g of the same carotenoid present in corn, determine which one it is by explaining your reasoning, using calculations.

The reaction between an aldehyde or ketone function with a diol is an acetalization, which forms cyclic acetals of the dioxolane family. This reaction can also be used to identify or quantify carotenoids.



Ethylene glycol Dioxolane

For example, the end of the acetalization reaction can be detected by infrared. After addition of 12.3 mL of ethylene glycol to 100.0 mL chanterelle concentrate, a peak attributable to the alcohol function is detected, synonymous with an excess of diol (only the carotenoid is considered to react with ethylene glycol in the chanterelle juice). The concentration of carotenoid in the chanterelle concentrate was previously determined by absorbance to be equal to 1.1 mol/L.

c) Which carotenoid is present in the chanterelle that gives it its characteristic orange colour? Support your answer with a mathematical reasoning.

($C_2H_6O_2$: ρ = 1,11 kg/L)

LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Éducation nationale,
de l'Enfance et de la Jeunesse

ACLg

UNIVERSITÉ DU
LUXEMBOURG

Fonds National de la
Recherche Luxembourg

CHAMBRE DE
COMMERCE
LUXEMBOURG

CHAMBRE DES SALARIES
LUXEMBOURG

andré losch
fondatioun

Draft Sheet