UNIVERSITAT DE BARCELONA

APPLIED CHEMISTRY II

Faculty of Chemistry

University of Barcelona

LABORATORY HANDBOOK

Print this guide on both sides of the page and bind the sheets together before bringing it with you on the first day of the laboratory course.
Do not bring loose sheets to the laboratory.

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PART 1

INFORMATION FOR STUDENTS

1.1. ABOUT ACII. EXTRACT FROM THE TEACHING PLAN

General Information

Course name: Applied Chemistry II (ACII)

Course code: 360759

ECTS credits: 6

Estimated learning time (total number of hours): 150 h

Face-to-face learning activities: 60 h

Laboratory-related learning activities (keeping a laboratory notebook, reviewing related theoretical questions and answering the questions in the manual): 30 h

Independent learning: 60 h

Pre-requisites and recommendations for this course

Pre-requisites: those required for the UB Degree in Chemistry

Recommendations: prior completion of Basic Chemistry I and Applied Chemistry I is strongly recommended.

Skills that this course is designed to develop

- Learning ability and responsibility (analytical skills, synthetic skills, the ability to apply theoretical knowledge to practical experiments / the ability to make decisions and to adapt to new situations).
- Sustainability (the ability to assess the social and environmental impact of actions taken / the ability to entertain integrated overall visions).
- Planning and organizational ability.
- The ability to explain phenomena and processes that occur related to basic aspects of chemistry.
- The ability to exhibit knowledge and understanding of the main aspects related to chemical terminology, nomenclature, conventions and units.
- The ability to solve qualitative and quantitative problems according to previously developed models.
- The ability to evaluate, interpret and synthesize data and chemical information.
- The ability to handle chemical products safely and to assess risk when using them.

Educational objectives of this course

Academic learning

- To consolidate basic concepts related to a reaction stoichiometry and limiting reagent recognition.
- To know the main type of chemical reactions: acid–base, redox, precipitation and complexation.
- To know the fundamentals and applications of basic laboratory operations.
- To know the conventional units for expressing physicochemical magnitudes.

- To recognize the number of significant figures of a magnitude and to express a magnitude with the proper significance.
- To recognize and express correctly the experimental error associated with the use of laboratory material and instruments.
- To know some of the properties of chemical products (density, viscosity or vapour pressure) and how these condition their handling.
- To know the laboratory material, apparatus and instruments and their characteristics.
- To know the basic safety standards of a chemical laboratory and the safety regulations related to handling the chemical products used in the laboratory: identification, safety labels, classification, chemical safety cards and environmental limit values.

Abilities and skills

- To use basic laboratory operations properly.
- To contextualize acquired knowledge.
- To express solution and mixtures composition in conventional units.
- To calculate the stoichiometry of the reactions: molar ratios, limiting reagent and yields.
- To express the results of calculations and experimental measurements correctly.
- To use and handle chemical products and laboratory material appropriately and according to safety standards.
- To write a correct report on the activities conducted in the laboratory and to organize a laboratory notebook properly.
- To apply correct laboratory quality management.
- To understand and use standard operating procedures encountered in the laboratory.
- To handle chemical waste generated in the laboratory properly.

Attitudes, values and criteria

- To display a consistently positive attitude during face-to-face sessions.
- To carry out the assigned tasks carefully.
- To carry out individual learning in a continuous way.
- To learn that chemical products, as potentially dangerous substances, must be handled with care.
- To take care of the material, apparatus and instruments in the laboratory.
- To make efforts to draft a laboratory notebook properly.
- To work cooperatively and in a group.
- To be aware of the importance of working responsibly, safely and hygienically in the laboratory, considering quality and environmental aspects.

Teaching methods and general organization

In this subject, laboratory practices are the main channel of transmission of knowledge. In the practical sessions, the students individually carry out experiments that are included in the laboratory handbook, as assigned by the teachers. To perform this experimental work properly, it is necessary for the student to devote a few hours to preparing the practical aspects and to consult the recommended bibliography. Students must understand the theoretical and practical aspects of the procedure and must be able to answer teacher questions satisfactorily. Within the directed work, the teacher can ask students to carry out specific work or specific tasks that the teacher will control and evaluate following the criteria set out at the beginning of the practical sessions. The student must keep a laboratory notebook where all the activities carried out in the laboratory are registered daily. The notebook must be completed in the laboratory and delivered to the teacher at the end of the practical session. The notebook will be returned to the student once it has been evaluated by the teacher.

Official assessment of learning outcomes

In these laboratory sessions, attendance is compulsory and only two absences will be accepted, provided there is a **valid and justifiable** reason.

Assessment of the student's laboratory activities is continuous and individual (and constitutes 60% of the final grade for the course). It will be based on the following criteria: attitude, tidiness and organization, safety consciousness, comprehension, maturity, learning and handling skills, prior preparation of each practical assignment, the presentation and discussion of results with the teaching staff and the laboratory notebook.

A written final examination related to the contents and activities carried out in the practical sessions (experimental work, knowledge of chemical reactivity, characterization of compounds, safety and waste management) accounts for the remaining 40% of the final grade for the course.

For English-language groups, both teaching staff and students are expected to communicate in English throughout the duration of the course. The English language ability of students (provided that it is within reasonable limits of comprehensibility) will not be taken into account when calculating the final grade for the course. Students who systematically fail to show a clear willingness to work in English will be penalized with respect to their grade.

Given the experimental nature of the subject, there is no single assessment option (*Avaluació única*).

Bibliography

Applied Chemistry II. Laboratory Handbook.

Atkins, P.; Jones, L. *Principios de Química. Los caminos del descubrimiento*. 5ª ed., Ed. Médica Panamericana, 2012 (Applied Chemistry and Basic Chemistry textbook).

Corbella Cordomí, M. *Els fonaments de la Química Bàsica 1*. Col·lecció OMADO, 2019.

Rodríguez Pérez, C. M.; Ravelo Socas, J. L.; Palazón López, J. M. *Técnicas de Organización y Seguridad en el Laboratorio*. Ed. Síntesis, 2005.

1.2. SAFETY REGULATIONS

LABORATORY SAFETY REGULATIONS IN THE FACULTY OF CHEMISTRY

REGULATIONS THAT MUST BE COMPLIED WITH

PERSONAL

- Smoking, drinking, eating or bringing food or drink into the laboratory is strictly prohibited.
- A laboratory coat and safety goggles must be worn at all times.
- Working alone in the laboratory is strictly prohibited.
- Long hair must be tied back at all times.
- Outside the laboratory, laboratory coats should not be worn in areas where there is food or drink.

ORGANIZATIONAL

- The maximum capacity established for the laboratory must not be exceeded.
- Work areas must always be kept clean and tidy.
- Food and drink must not be kept in areas where chemical products are stored or handled.
- All chemicals and waste products must be labelled and packaged correctly.
- Any chemical spills must be cleaned up immediately.

EQUIPMENT

- The laboratory must be equipped with suitable fire extinguishers and fire blankets.
- Exit doors must always be in working order and free from any obstruction.
- Obstacle-free evacuation routes must be clearly indicated.
- Signs indicating danger or hazards must be posted where necessary.
- The laboratory must be equipped with suitable absorbent products for use in case of spills.
- The laboratory must be equipped with containers for all waste products.
- The laboratory must be equipped with a first aid kit.

GOOD LABORATORY PRACTICES

CLOTHING AND HYGIENE

- Contact lenses must not be worn.
- Closed footwear is required.
- Clothes that cover arms and legs should be worn (avoid wearing shorts or short skirts. Do not roll up lab coat sleeves).
- Tights must not be worn.
- Students should wash their hands every time they have direct contact with chemical products, after an experiment and before leaving the laboratory.
- Laboratory coats should be washed separately from other clothing.

IDENTIFICATION OF CHEMICAL PRODUCTS AND WASTE

- Product labels must show hazard pictograms, risk phrases (R-phrases) and safety phrases (S-phrases).
- Labels must not be modified under any circumstances.
- One label must not be stuck over another one under any circumstances.
- An unidentified product must automatically be considered waste and treated as such.

HANDLING CHEMICAL PRODUCTS AND WASTE

- The laboratory must have a safety data sheet for all chemical products used.
- Products and chemical waste must be handled with great care, and direct contact with the skin should be avoided.
- A suitable apparatus must be used to fill pipettes with liquids (rubber bulb, Pi-Pump, etc.).
- Suitable personal protection equipment (PPE) must be worn.
- Toxic, flammable or corrosive products must be handled in a fume cupboard.
- Chemical products or waste must never be smelled or tasted.
- Before a chemical product is used, the label must be read carefully and the safety indications followed.
- Surfaces and materials should not be touched with contaminated gloves.
- Chemical products and waste must always be transported under the safest conditions possible. A suitable trolley or a plastic box with handles should be used.
- Chemical products and waste should always be transported in a goods lift and never in one that is used by the general public.
- Gas cylinders must be transported on suitable trolleys; they should never be rolled or dragged. During transport, cylinders must have the valve shut.
- Gas cylinders must be stored in a vertical position and should be attached to a wall or a solid surface by means of a clamp, chain or other device to prevent them from falling.
- Waste must be disposed of as soon as it is generated in order to prevent confusion and potential accidents.
- Solid and liquid waste must be collected separately, according to the established criteria for separation.
- Waste from different categories must not be mixed, to prevent potential unwanted reactions.
- The label on a container must be read carefully before waste is thrown into it.
- Only the necessary amount of reagent should be used: any excess becomes waste. It must never be put back into its original container.
- Do not fill waste containers to more than 90% of their capacity, to avoid accidents such as splashes, spills or excess pressure.

STORAGE OF CHEMICAL PRODUCTS AND WASTE

- The stock of chemical products must be kept at a minimum.
- When chemical products and waste are stored, consider how hazardous the products are, whether they are incompatible, how long they can be stored, and the conditions of confinement and isolation. Alphabetical order should only be used for groups of compatible products.
- The number of chemical products kept in the laboratory should be as low as possible. Flammable products must be kept in safety cabinets, and the criteria of compatibility must be followed.
- Refrigerators must be specifically designed to prevent the risk of explosion. Domestic refrigerators should not be used to store chemical products.
- Gas cylinders under pressure must be kept in suitable safety cabinets or on premises that are separate from (or external to) the laboratory.
- Any fixed installations for the distillation of solvents must be situated in a separate room or within a fume cupboard.
- Waste must be stored separately from chemical products.

Bear in mind that at all times:

1. During practical sessions, all students must wear a **laboratory coat**. It must be easy to unfasten and preferably made of cotton.
2. **Safety glasses or goggles** should be worn whenever students are in any part of the laboratory. Students should not use contact lenses, even if they are wearing safety glasses or goggles.
3. All personnel in the laboratory must know the location of fire extinguishers, fire blankets, safety showers, eyewash stations and emergency exit from the laboratory and from the floor of the building.
4. Students must wash their hands after they have finished an experiment and before they leave the laboratory.
5. Running or playing in the laboratory is strictly prohibited. Do not walk too quickly or push past others: you might cause an accident.
6. Long hair should be tied back.
7. Fume cupboards (with the extraction system activated) must be used whenever students work with toxic substances or those that are respiratory irritants or otherwise cause discomfort.
8. Any experiment that is not in the practical handbook, or any change in the quantities of reagents or procedure of an experiment, must not be carried out without the express permission of the teaching staff.
9. Students must avoid contact between any product or solvent and their skin. If accidently contaminated with a product or solvent, clean it off immediately with water and soap.
10. All benches and fume cupboards must be kept clean and tidy: it makes it easier to work safely and potentially hazardous breakages and spills are less likely. Bags or outerwear must not be brought into the laboratory.
11. Flammable substances must not be heated in open recipients over a heating mantle or hot plate (the hot vapours are denser than air and could ignite in contact with the electrical element of the mantle or hot plate). The safest way to heat flammable substances is in a water bath. Never heat flammable substances in a closed recipient.
12. You should not enter the laboratory until a member of the teaching staff arrives. Do not stay in the laboratory once the teaching staff has left. Never work alone in the laboratory.
13. Waste must be stored in the recipients available for this purpose (**see Section 1.6**). **Never throw waste down the sink** or in the bins without the teaching staff's permission. Listen carefully to the teaching staff's instructions on the first day of laboratory work, consult the information in the handbook for each practical exercise, and if in doubt consult the teaching staff.
14. Excess reagent should never be put back into the original container. Many reagents are expensive so measure them out very carefully.
15. All students are responsible for the equipment in their bench. At the end of a practical session, your bench should contain all the equipment that was in it at the start of the session, which corresponds to that listed in this handbook.

1.3. KEEPING A LABORATORY NOTEBOOK

The experimental procedure as well as the results of all experiments carried out in the laboratory should be recorded in a laboratory notebook. This serves as a written record of the experiment carried out and should provide another person sufficiently detailed information to repeat a given experiment.

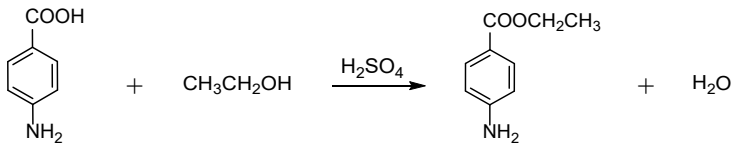
Some blank pages should be left at the start of the notebook for the index of contents. The front pages should also contain the name and telephone of the owner in case the notebook is mislaid. To avoid loss or deterioration, the notebook should be bound (so that pages do not fall out), with hard or laminated covers (so that it does not deteriorate with use). The pages should be numbered by the student.

The laboratory notebook should be written in the lab and must be permanently up to date. It can be completed at home but cannot be copied to a clean version. You have to write with a pen, and you cannot use Tipp-Ex or cross things out so you cannot see what was written. Pages cannot be ripped out and must be understandable (take care of the writing, vocabulary, spelling, etc.).

Each experiment should be recorded in the laboratory notebook as follows:

1. **Date.** A date is required to identify when the experiment was carried out. It is a good idea to write down the date every day when you start work.
2. **Title.** A title helps you to find an experiment quickly.
3. **Objectives.** The objectives of the experiment should be stated clearly and concisely (do not copy the laboratory handbook!).
4. **Bibliography.** All scientific literature or textbooks consulted in order to understand and carry out the experiment should be cited clearly and accurately. Write your bibliographic references in the same format as that used in this handbook.
5. **Chemical equations.** Write the chemical equations for all the reactions that are performed, as this enables rapid visual recognition of the reagents involved, their chemical structure, and the stoichiometry of the process.

   In the chemical equation, under each reagent and/or product, indicate the molecular mass and physical properties of interest (melting point, density, etc.). In addition, very briefly state the reaction conditions so that they can be identified rapidly.



Molecular weight (g/mol)	137.14	46.07	165.19
Density (g/mL)	-	0.79	-
Purity (%)	99	95	-
Amount used	5.00 g	15 mL	5.96 g (expected)
Millimoles	36	244	36
Molar ratio	1	6.8	1
Melting point (ºC)	187	−114	88
Boiling point (ºC)	340	78	311

6. **Safety and waste disposal.** You should include information about safety and the hazards of reagents and products, and describe safe procedures for manipulating reagents and products as well as treating waste generated in the practical exercise.
7. **Diagram of the experimental procedure.** You should draw a diagram or working outline of the complete experimental procedure that will help you to organize the work in each session and have a global vision of the whole experiment.
8. **Experimental observations, diagram of apparatus.** You should not copy the procedure described in the handbook, but rather note down how the experiment is carried out in the laboratory. You should note any phenomena that you observe (changes in colour, the appearance of precipitates or turbidity, an increase in temperature, etc.). Often, you will need to draw a diagram of the apparatus or set-up that you use in the experiment, particularly if it is special or unusual.
9. **Results, calculations and yields.** The laboratory notebook must contain all notes on weights, tares, yields and calculations that have been obtained or carried out during the practical exercise. The values of required parameters or physical constants (melting point, boiling point, rate constant, enthalpy of the reaction, etc.) must be determined.
10. **Conclusions.** In this section, the results must be analysed, and relevant conclusions drawn.
11. **Answers to questions.** All the questions at the end of each experiment must be answered in the notebook.
12. **Summary table of reagents and products.** At the end of the notebook include a summary table containing all the reagents and products that have been used. In the table, the name and the molecular formula of each species must be included.

Compound name	**Molecular formula**
Nitric acid	HNO_3
Sulphuric acid	H_2SO_4
…	…

1.4. PLANNING LABORATORY WORK

Students must always bring the equipment they need for personal use to the undergraduate laboratory: safety goggles, laboratory coat, spatula, glass marking pen, calculator and a square piece of fabric that may serve as a dishcloth or small towel. Remember that you are not allowed to enter the laboratory with bags or outerwear.

You must determine in advance which practical exercise you will be assigned next, according to the course schedule that you will be given. If in doubt, you should consult the teaching staff before you finish the practical exercise that you are currently working on.

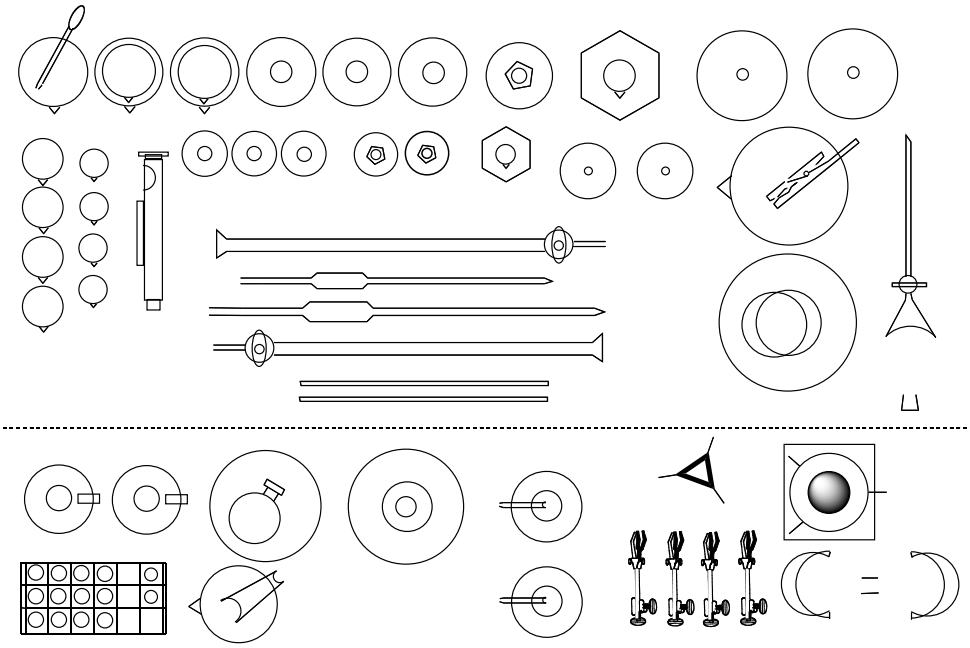
Study the practical exercise carefully and answer all questions in this handbook that relate to it before you start the experiment. The teaching staff may ask these questions at any time. This is individual work that must be completed outside laboratory time.

Before starting the experiment, you must understand the objectives of the exercise and the theoretical basis of the reactions and calculations involved, as well as the reason for each of the laboratory operations that must be undertaken.

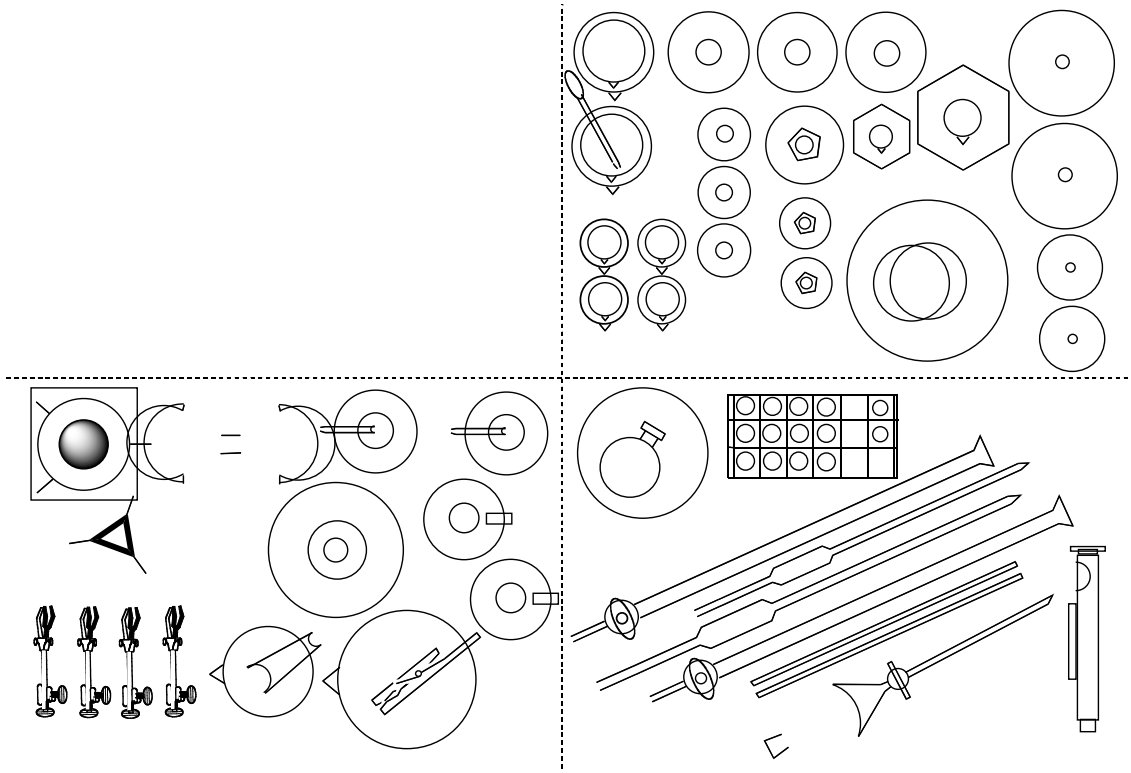
Before handling reagents or assembling apparatus, you must complete the first seven sections of the laboratory notebook (see Section 1.3 above).

1.5. LABORATORY EQUIPMENT FOUND IN THE BENCH CUPBOARDS

CUPBOARD CONTENT (TOP SHELF)



CUPBOARD CONTENT (BOTTOM SHELF)



CATALÀ		ENGLISH
Vas de precipitats 600 mL	2	Beaker
Vas de precipitats 400 mL	2	
Vas de precipitats 250 mL	1	
Vas de precipitats 100 mL	4	
Vas de precipitats 50 mL	4	
Matràs d'Erlenmeyer 250 mL	3	Erlenmeyer (conical) flask
Matràs d'Erlenmeyer 100 mL	2	
Matràs d'Erlenmeyer 50 mL	1	
Matràs aforat 250 mL	3	Volumetric flask
Matràs aforat 100 mL	2	
Embut de forma alemanya 120 mm	2	Conical funnel
Embut de forma alemanya 60 mm	2	
Embut de decantació 250 mL (+ tap)	1	Separatory funnel
Matràs de Kitasato 500 mL	2	Suction (side-arm) flask
Embut de Buchner	1	Büchner funnel
Baló 250 mL coll ample	1	Round-bottom flask
Proveta 100 mL	1	Measuring cylinder
Proveta 10 mL	1	
Pipeta 2 mL	1	Pipette
Pipeta 5 mL	1	
Pipeta 10 mL	1	
Pipeta 20 mL	1	
Pipeta 25 mL	1	
Gradeta	1	Test tube rack
Tub d'assaig	10	Test tube
Tub de centrifugadora	2	Centrifuge tube
Bureta 25 mL	2	Burette
Morter	1	Mortar
Comptagotes	2	Dropper
Vareta de vidre	2	Glass rod
Cristal·litzador	1	Crystallizer
Vidre de rellotge 120 mm	2	Watch dish
Vidre de rellotge 60 mm	2	
Càpsula de Petri	1	Petri dish
Càpsula de porcellana	1	Porcelain vessel
Flascó rentador	2	Plastic wash bottle
Pinça d'estendre roba de fusta	2	Clamp
Aspirador pipetes (Pi-Pump)	1	Pipette pump (Pi-Pump)
Pinça	4	Clamp
Nou	4	Clamp holder

1.6. WASTE MANAGEMENT PLAN IN THE LABORATORY

PLA DE GESTIÓ DE RESIDUS DE LA DOCÈNCIA PRÀCTICA

Ensenyament	**Grau de Química**
Secció	**Laboratoris Bàsics**
Assignatura	**Química Aplicada II**

Edició: **Unitat de Qualitat, Medi Ambient i Seguretat**
Facultat de Química
Novembre 2021

Introducció

La Facultat de Química reconeix en la política de qualitat, medi ambient i seguretat el compromís amb la preservació del medi ambient i amb el desenvolupament sostenible de la societat. En el cas particular de la Facultat, es dedica un esforç especial a la minimització de les quantitats de residus de laboratori generats i a la reducció de la seva perillositat i el seu impacte ambiental.

En aquest sentit, existeix la necessitat de gestionar els residus de laboratori de forma separada, de la mateixa manera que es fa amb els residus domèstics, atenent a criteris ambientals i de seguretat, essent conscients en tot moment que es tracta de residus especialment contaminants i perillosos per a la salut i el medi ambient.

Aquesta guia presenta de forma clara i esquemàtica la gestió dels diferents residus que generareu a través de les pràctiques d'aquesta assignatura atenent a criteris d'eficiència, seguretat i respecte pel medi ambient. Per a cada pràctica disposareu d'una fitxa amb la relació de residus que es generen i la seva gestió, en la que s'indica el contenidor de destí que correspon a cadascun d'ells.

Finalment, recordeu que no està permès abocar cap residu per l'aigüera excepte en aquells casos en què us ho indiqui aquesta guia o el vostre professor. En cas de qualsevol dubte, consulteu sempre al vostre professor responsable com heu de gestionar correctament el residu.

PRÀCTICA 1. REACCIONS QUÍMIQUES EN TUB D'ASSAIG			
Residu	**Contenidor destí**	**Etiqueta**	**Nº Bidó**
Solució àcida AgCl	Líquids boca estreta	**Metalls pesants: solucions àcides**	**1**
Solució àcida Pb^{2+} i $PbCl_2$			
Solució $[Cu(NH_3)_4]^{2+}$			
Solució Mn^{2+}			
Solució que conté MnO_4^-			
Solució Pb^{2+} i sòlid $PbCrO_4$	Líquids boca estreta	**Solucions de Cr(VI)**	**2**
Solució aquosa $PbCrO_4$			
Solució de Hg^0/Hg^{2+}	Líquids boca estreta	**Substàncies molt tòxiques: mercuri metàl·lic i amalgames de mercuri**	**3**
Paper filtre contaminat Hg^0	Sòlids boca ample		**A**
Paper filtre contaminat	Bidó blau	**Material contaminat amb productes químics (guants, papers.....)**	
HCl i paper d'alumini (un cop dissolt tot el paper d'alumini)	Líquids boca estreta	**Compostos inorgànics d'altres metalls**	**5**

PRÀCTICA 2. VOLUMETRIA ÀCID-BASE	
Residu	**Contenidor Destí**
Solució de NaOH, $HOOCC_6H_4COOK$ i fenolftaleïna	Abocar a l'aigüera amb excés d'aigua

PRÀCTICA 3. COMPOSTOS DE COORDINACIÓ DE NÍQUEL (II) I COURE (II)			
Residu	**Contenidor destí**	**Etiqueta**	**Nº Bidó**
Productes sòlids obtinguts	Sòlids boca ampla	**Metalls pesants: compostos sòlids**	**B**
Filtrat preparació $[Ni(NH_3)_6]Cl_2$	Líquids boca estreta	**Compostos amoniacals**	**12**
Filtrat preparació $[Ni(en)_3]S_2O_3$.	Líquids boca estreta	**Dissolucions aquoses orgàniques o d'alta DQO**	**7**
Filtrat preparació $[Cu(en)_2]SO_4$.	Líquids boca estreta	**Dissolvents no halogenats**	**9**

PRÀCTICA 4. SÍNTESI DE L'ASPIRINA			
Residu	**Contenidor destí**	**Etiqueta**	**Nº Bidó**
Solució del primer filtrat amb Büchner	Líquids boca estreta	**Àcids orgànics no halogenats**	**8**
Solucions àcides resultants de les purificacions			
Solució de Fe^{3+}	Líquids boca estreta	**Metalls pesants: solucions bàsiques o neutres**	**6**
Paper de filtre contaminat	Bidó blau	**Material contaminat amb productes químics (guants, papers.....)**	
Capil·lars de vidre	Sòlids boca ample	**Material contaminat amb productes químics: vidre punxant**	
Àcid acetilsalicílic	Líquids boca estreta	**Sòlids orgànics no halogenats**	**C**
Plaques de CCF	Contenidor específic	**Material contaminat amb productes químics: plaques CCF**	**H**

PRÀCTICA 5. SEPARACIÓ DE BARREGES LÍQUIDES PER DESTIL·LACIÓ			
Residu	**Contenidor destí**	**Etiqueta**	**Nº Bidó**
Àcid acètic glacial sobrant	Líquids boca estreta	**Àcids orgànics no halogenats**	**8**
Fraccions recollides			
Àcid acètic que queda al baló			

PRÀCTICA 6. EXTRACCIÓ DE LA CAFEÏNA D'UNA BEGUDA DE COLA			
Residu	**Contenidor destí**	**Etiqueta**	**Nº Bidó**
Fases aquoses de les decantacions	Líquids boca estreta	**Dissolucions aquoses orgàniques o d'alta DQO**	**7**
Filtre de plecs amb Na_2SO_4	Bidó blau	**Material contaminat amb productes químics (guants, papers.....)**	
Capil·lars de vidre	Sòlids boca ample	**Material contaminat amb productes químics: vidre punxant**	
Restes diclorometà	Líquids boca estreta	**Dissolvents halogenats**	**10**
Residus de dissolvent rotavapor			

PRÀCTICA 7. REACCIÓ A REFLUX: SÍNTESI DE L'ACETAT D'ISOAMIL			
Residu	**Contenidor destí**	**Etiqueta**	**Nº Bidó**
Àcid acètic glacial	Líquids boca estreta	**Àcids orgànics no halogenats**	**8**
Fase aquosa àcida	Líquids boca estreta	**Dissolucions aquoses orgàniques o d'alta DQO**	**7**
Fase aquosa del rentat amb $NaHCO_3$			
Fase aquosa del rentat amb aigua			
Acetat d'isoamil (oli de plàtan)	Líquids boca estreta	**Dissolvents no halogenats**	**9**
Filtre de plecs	Bidó blau	**Material contaminat amb productes químics (guants, papers.....)**	
Na_2SO_4 sòlid	Sòlids boca ampla	**Compostos inorgànics d'altres metalls**	**B**
Restes de diclorometà	Líquids boca estreta	**Dissolvents halogenats**	**10**
Residus de dissolvent rotavapor			

PRÀCTICA 8. ESPECTRES D'ABSORCIÓ. ÚS D'UN COLORÍMETRE I COMPROVACIÓ DE LA LLEI DE LAMBERT-BEER			
Residu	**Contenidor destí**	**Etiqueta**	**Nº Bidó**
Solucions de permanganat	Líquids boca estreta	**Solucions de Mn(VII)**	**4**

PRÀCTICA 9. ESTANDARDITZACIÓ D'UNA SOLUCIÓ DE PERMANGANAT PER VOLUMETRIA REDOX			
Residu	**Contenidor destí**	**Etiqueta**	**Nº Bidó**
Oxalat de sodi sòlid	Sòlids boca ample	**Sòlids orgànics no halogenats**	**C**
Solució de permanganat	Líquids boca estreta	**Solucions de Mn(VII)**	**4**
Dissolució de Mn^{2+}	Líquids boca estreta	**Metalls pesants: solucions àcides**	**1**

PRÀCTICA 10. ENTALPIA D'UNA REACCIÓ DE NEUTRALITZACIÓ	
Residu	**Contenidor destí**
Solució HCl i NaOH amb fenolftaleïna	Abocar a l'aigüera amb excés d'aigua

PRÀCTICA 11. PILES: PROCESSOS I FORÇA ELECTROMOTRIU			
Residu	**Contenidor destí**	**Etiqueta**	**Nº Bidó**
Solucions que continguin $Cu^{2+}/Zn^{2+}/Fe^{2+}/Fe^{3+}$	Líquids boca estreta	**Metalls pesants: solucions neutres i bàsiques**	**6**
Solució de KCl + Fe^{3+} + fenolftaleïna			
Dissolució de HCl i Zn	Líquids boca estreta	**Metalls pesants: solucions àcides**	**1**
Dissolució d'HNO_3 i Cu			
Solució de KCl pont salí	Abocar per l'aigüera amb excés d'aigua		
Aigua d'esbandir els elèctrodes	Líquids boca estreta	**Metalls pesants: solucions àcides**	**1**
Clau de ferro	Contenidor específic	**Fe**	**D**
Papers de filtre o cotons del pont salí	Bidó blau	**Material contaminat amb productes químics (guants, papers.....)**	

PRÀCTICA 12. DETERMINACIÓ POTENCIOMÈTRICA DE L'ACIDESA TOTAL D'UN VINAGRE I ESTIMACIÓ DEL pK_a DE L'ÀCID ACÈTIC	
Residu	**Contenidor destí**
HCl + H_2O	Abocar a l'aigüera amb excés d'aigua
Acètic + H_2O	
NaCl + H_2O	
Acetat de sodi + H_2O	
NH_3 + H_2O	
NaOH + H_2O	
Vinagre	
Dissolucions valorades	

Acètic + Acetat + H_2O	Combineu els residus i aboqueu a l'aigüera amb excés d'aigua
Acètic + Acetat + HCl	
Acètic + Acetat + NaOH	

PRÀCTICA 13. ESTUDI CINÈTIC DE LA REACCIÓ D'UN COLORANT ALIMENTARI AMB LLEIXIU	
Residu	**Contenidor destí**
Solucions que continguin el colorant alimentari	Abocar a l'aigüera amb excés d'aigua

PART 2

LABORATORY EXPERIMENTS

EXPERIMENT 0 - PREPARATION OF STOCK SOLUTIONS

Specific objectives

Preparation of stock solutions.

Use of volumetric equipment.

Expression of the composition of solutions and mixtures. Stoichiometric calculations.

Experimental Procedure

Do the necessary calculations to prepare 0.5 L or 1 L (ask the teaching staff) of each of the following solutions:

- 0.1 M sodium hydroxide solution
- 0.1 M sodium acetate solution
- 0.1 M sodium chloride solution
- 0.1 M zinc(II) sulphate solution
- 0.1 M copper(II) sulphate solution
- 0.2 M potassium hexacyanoferrate(II) solution, $K_4[Fe(CN)_6]$
- 0.2 M potassium hexacyanoferrate(III) solution, $K_3[Fe(CN)_6]$
- 3 M potassium chloride solution

Consider the purity of all reagents in your calculations and that some compounds are hydrated salts like, for instance, $CuSO_4 \cdot 5\ H_2O$.

Prepare the assigned solution following the teacher's instructions.

EXPERIMENT 1 - CHEMICAL REACTIONS IN TEST TUBES

Specific objectives

Test tube handling. Operation on a semi-micro scale.

Precipitation, centrifugation and filtration.

Study of the influence of some variables on the speed of chemical reactions.

Individual work to be done before starting the experiment

Read Section I (*Soluciones acuosas y precipitación*) and K (*Reacciones de oxidorreducción*) of the chapter *Fundamentos* (pages F65-F70 and F77-F83) in the textbook *Principios de Química. Los caminos del descubrimiento*.

Review Chapter 14 (*Cinética Química*) in the textbook *Principios de Química. Los caminos del descubrimiento*.

Introduction

Many of the tests that are often carried out in the laboratory are done on a semi-micro scale, in other words, using very little of the sample. Specifically, the separation and identification of the cations present in complex mixtures can be performed this way. The most common laboratory equipment used for this is the test tube. It is therefore essential to know how to manipulate and heat test tubes correctly. Moreover, you should also learn how to filter and centrifuge at this scale of work.

Chemical kinetics is the part of chemistry that studies the path along which reactants are converted into reaction products, the speed at which chemical reactions occur and the factors that govern the speed of chemical transformations. Even when working at a reduced scale, the speed of chemical reactions in solution depends on the concentration of the reactants, the temperature and the presence, or absence of catalysts. Furthermore, in heterogeneous systems like, for example, the attack of acids on some metals, the specific surface of the solid reactant dramatically affects the speed at which the reaction proceeds.

Experimental procedure

1. Study of the reactivity of some metallic cations.

Ag^+ cation: Add 0.5 mL of 2 M HCl to 0.5 mL of a silver nitrate solution; a white precipitate appears. Then, slowly add 2 mL of 2 M NH_3; the soluble complex $[Ag(NH_3)_2]^+$ is formed. Acidification with a few drops of 2 M HNO_3 causes AgCl to precipitate again.

Hg_2^{2+} cation: Add, dropwise, 1 mL of 2 M HCl to 1 mL of a $Hg_2(NO_3)_2$ solution; a white precipitate appears. Then, slowly add 1 mL of 2 M NH_3 and observe that the precipitate quickly darkens due to the formation of metallic mercury. Notice that in the presence of ammonia, mercury(I) dismutates:

$$Hg_2Cl_2 + 2\ NH_3 \rightarrow Hg + Hg(NH_2)Cl + NH_4Cl$$

in other words, mercury(I) reduces and oxidizes simultaneously: $Hg_2^{2+} \rightarrow Hg + Hg^{2+}$.

Pb^{2+} cation: Add, dropwise, 1 mL of 2 M HCl to 1 mL of a $Pb(NO_3)_2$ solution; a white precipitate appears. Then, slowly add 2 mL of 2 M NH_3 and observe that the precipitate of lead(II) chloride does not dissolve. Centrifuge and decant the supernatant liquid. Remember that centrifugation always requires the use of two centrifuge tubes: the first contains the sample while the second is filled with water until the weight of both tubes is approximately the same. Add 2 mL of water to the centrifuged solid and heat the resulting suspension. Heat the test tube at the meniscus level, with continuous shaking and moving it in and out of the Bunsen flame to avoid uncontrolled boiling. Do not heat test tubes filled to more than one third of their volume. Notice that the lead(II) chloride is soluble in hot water but it precipitates, in the form of sheets, at lower temperatures.

Cu^{2+} cation: Add a few drops of 2 M HCl to 1 mL of a 0.25 M $CuSO_4$ solution. The Cu^{2+} cation does not precipitate in the presence of Cl^-. Then, add a few drops of 2 M NH_3; the formation of the dark blue soluble complex $[Cu(NH_3)_4]^{2+}$ is observed.

Mn^{2+} cation: Add a very small amount (spatula tip) of $NaBiO_3$ to 3 mL of a 0.25 M H_2SO_4 solution. Then, add a few drops of a 0.1 M $MnSO_4$ solution. The solution becomes pink due to the formation of permanganate. The reaction that takes place is:

$$2\ Mn^{2+} + 5\ BiO_3^- + 4\ H^+ \rightarrow\ 2\ MnO_4^- + 5\ BiO^+ + 2\ H_2O$$

Cr^{3+} cation: Add, dropwise, 2 M NaOH to 1 mL of a 0.25 M $Cr(NO_3)_3$ solution until a strongly basic medium is achieved. First, a greenish precipitate of $Cr(OH)_3$ is observed, which readily dissolves in an excess of OH^- due to the formation of the dark green soluble complex $[Cr(OH)_6]^{3-}$. Then, add a few drops of H_2O_2 (3% v/v in water) to 1 mL of the previous solution and warm the resulting solution carefully. The solution becomes yellow due to the presence of the chromate ion. Let the solution cool down to room temperature and confirm the presence of the chromate ion by adding a few drops of a 0.05 M $Pb(NO_3)_2$ solution. The formation of a yellow precipitate is observed.

2. Separation and identification of the metallic cations present in a complex mixture.

2.1. Consider a solution containing the following metallic cations: Ag^+, Pb^{2+}, Hg_2^{2+} and Cu^{2+}. On the basis of the reactions studied in the previous section and after reading the protocol that you will follow in the next subsection (2.2), draw a flux diagram showing the separation and subsequent characterization of the different cations in this solution. Discuss your flux diagram with the teaching staff. The teacher will show you which solution should be used in this experiment.

2.2. Add, dropwise, 2 M HCl to 5 mL of the solution containing the metallic cations until the formation of fresh precipitate is no longer observed. Filter the precipitate and collect the filtrate in a beaker labelled as *Filtrate 1*. Double check that the precipitation has been completed by adding a few drops of 2 M HCl to the filtrate. If a new white precipitate appears, add one or two extra drops of HCl and filter the solid formed (use the same filter paper and collect the filtrate in the beaker labelled *Filtrate 1*). Finally, wash the precipitate thoroughly with cold water, acidified with a few drops of 2 M HCl (also collect this filtrate in the beaker labelled *Filtrate 1*). Observe and write down the colour of *Filtrate 1*. Keep *Filtrate 1* to identify the metallic cation it contains later.

Add 5 mL of boiling water to the white precipitate. Collect the filtrate in a test tube labelled as *Filtrate 2*. The collected filtrate can be reheated and added again to the precipitate to make sure that all the compounds soluble in hot water have dissolved. Write down what happens when *Filtrate 2* is cooled down to room temperature. Keep *Filtrate 2* to identify the metallic cation it contains later.

Add 3 mL of 2 M NH_3 to the remaining precipitate and collect the filtrate in a new test tube labelled as *Filtrate 3*. Write down the changes that occur to the solid residue.

Add a few drops of 2 M HNO_3 to *Filtrate 3*. Write down the changes observed.

Run appropriate tests to identify the metallic cations that are present in *Filtrate 1* and *Filtrate 2*.

According to the results obtained, what is the composition of the sample? Write and balance all the chemical reactions that take place in each step of the process.

3. Influence of some variables on the speed of chemical reactions.

3.1. Concentration of the reactants

Place 3 mL of 4 M HCl in a test tube. In another tube, put 3 mL of 2 M HCl. Using scissors, cut two squares (4 × 4 cm) of aluminium foil. Fold the squares with your fingers to obtain two compact balls and put one in each test tube. Write down and explain what you observe. Which chemical reactions take place in this experiment?

3.2. Specific surface area

Place 3 mL of 4 M HCl in each of two test tubes. Cut 2 squares (4 × 4 cm) of aluminium foil. Fold the squares into a cylindrical rod and a compact ball. Put the cylindrical rod in one test tube and the compact ball in the other. Write down and explain what you observe. Which chemical reactions take place in this experiment?

3.3. Temperature

Place 1 mL of a 0.1 M sodium oxalate solution in each of two test tubes and add 1 mL of 0.25 M H_2SO_4. Shake the tubes gently to homogenize the contents. Heat one of the test tubes slightly (up to 50-60 ºC) and keep the other at room temperature. Add 10 drops of a 0.02 M $KMnO_4$ solution to each tube. Write down and explain what you observe. Which chemical reactions take place in this experiment?

3.4. Presence of a catalyst

Place 1 mL of a 0.1 M sodium oxalate solution in each of two test tubes and add 1 mL of 0.25 M H_2SO_4. Shake the tubes gently to homogenize the contents. In one of the tubes, add a few crystals of manganese(II) sulphate and stir the tube until they dissolve completely. Add 10 drops of a 0.02 M $KMnO_4$ solution to each test tube. Write down and explain what you observe. Which chemical reactions take place in this experiment?

Safety and waste disposal

Dispose of the waste in the designated areas in the lab, as indicated in "*Pla de Gestió de Residus de la Docència Pràctica*" (see page 21).

Questions

1. Draw the Lewis structures of the following substances: H_2SO_4, HNO_3 and NH_3.
2. Write and balance all the chemical reactions that take place in Sections 1, 2 and 3 of this experiment. You should answer this question while performing the experiment. Indicate the type of reaction (precipitation, redox, formation of a complex, etc.) in each instance. For the redox reactions, write the half-reactions and the global reaction.
3. Explain why the AgCl precipitate dissolves when treated with NH_3 and precipitates again when HNO_3 is added to the solution.
4. How do the concentration of the reagents and the temperature influence the reaction rate? Is the reaction rate of a heterogeneous reaction affected by the specific surface area?
5. What is a catalyst? Give some examples.
6. What is the role of $MnSO_4$ in the reaction between sodium oxalate and potassium permanganate?

EXPERIMENT 2 – ACID–BASE TITRATION

Specific objectives

Preparation of solutions. Use of volumetric equipment. Weighing substances.

Determination of the exact concentration of HCl and NaOH solutions. Standardization.

Use of chemical and physical indicators (pH-meter).

Independent work to be done before starting the experiment

Read Section L (*Estequiometría*) of the chapter *Fundamentos* (pages F85-F93) in the textbook *Principios de Química. Los caminos del descubrimiento*.

Read the section *Titulaciones* in Chapter 12 (pages 483-496) of the textbook *Principios de Química. Los caminos del descubrimiento*.

Read Chapter 3 (*L'error experimental*) in the textbook *Anàlisi química quantitativa* (Harris, D. C. 6ª ed., Ed. Reverté, 2006).

Draw a diagram of the experimental procedure and discuss it with the teaching staff.

Introduction

In chemical analysis, the term "to determine" or "determination" means establishing the quantity or concentration of a specific substance (the "analyte") in a sample. There are several methods and techniques to determine an analyte. Among them, titrimetric analysis (or "titrimetry") is quantitative analysis based on the complete reaction of the analyte in the sample (the "titration") with a chemical substance (the titrating standard or standardized solution).

In titrimetric analysis, the concentration of the analyte in the sample is calculated from the measurement of the volume of standard solution necessary to make the analyte in the titrated sample react completely. This volume can be measured thanks to an additional chemical species or physical device (the "indicator") that is also present in the titrated solution. A chemical indicator changes its colour when the volume of standard solution needed to make the analyte react completely is reached, thereby allowing its measurement.

In titrimetric analysis, the sample (containing both, the analyte and the indicator) is placed in an Erlenmeyer flask (also known as "conical flask") and the volume of the standard solution is measured by means of a burette (or "buret" in American English) (Figure 1).

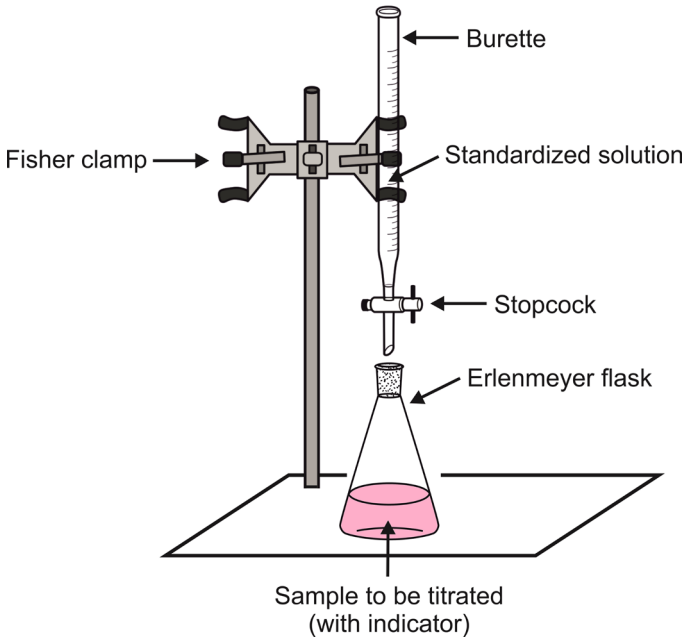


Figure 1. Experimental setup used for titration.
(Adapted from https://commons.wikimedia.org/wiki/File:Acid-base-titration-fr.svg)

Standard solutions may be prepared in several ways. When highly pure chemical substances are available, the standard solution is prepared using the exact weight of the calculated quantity of this substance, followed by its dissolution into the appropriate volumetric flask. A standard solution prepared in this way is known as a primary standard. Usually, a primary standard should have a purity higher than 99.9% and should be stable when faced with the carbon dioxide and water vapour in the atmosphere.

When chemical substances fulfilling these requirements are not available, it is necessary to determine the exact concentration by means of a titration process against a primary standard (the "standardization process").

Sodium hydroxide solutions are used as standard solutions for the determination of acid analytes in titrimetric analysis. As sodium hydroxide is not a primary standard, it must be standardized using a primary standard. Usually, potassium hydrogen phthalate ($HOOCC_6H_4COOK$, Figure 2*a*), which behaves as a weak acid when in contact with sodium hydroxide, is a suitable primary standard to standardize sodium hydroxide solutions. In these titrations, phenolphthalein is used as a chemical indicator (Figure 2*b*).

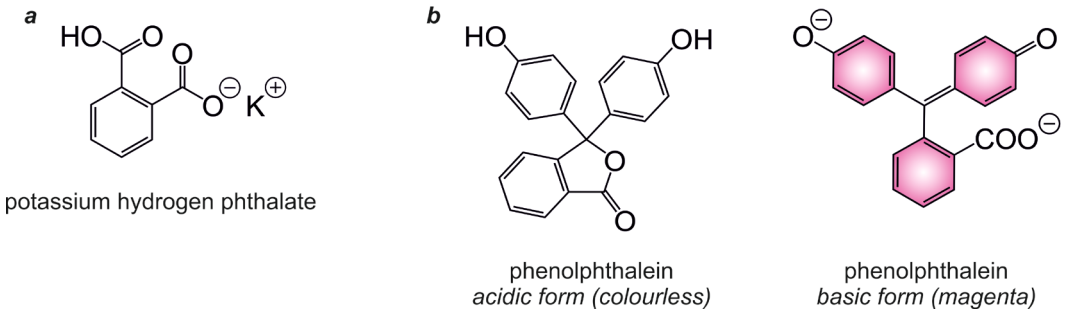


Figure 2. Chemical structures of potassium hydrogen phthalate (***a***), a primary standard, and the acidic and basic forms of phenolphthalein (***b***), an indicator.

Experimental procedure

1. Preparation of a 1.5 M hydrochloric acid solution.

Calculate the volume required to prepare 250.00 mL of a 1.5 M HCl solution. Measure this volume with a 100 mL cylinder and add it to a 250.00 mL volumetric flask. Add more water to the volumetric flask, stir and set the meniscus to the volume mark, as shown in the Figure 3. The prepared solution must be preserved because it will be used later, in Experiment 10.

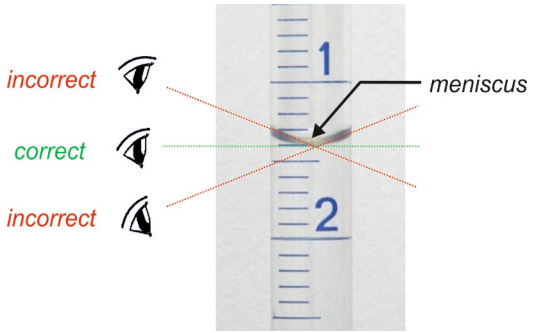


Figure 3. Setting the meniscus to the volume mark.

2. Preparation of a 1.5 M sodium hydroxide solution.

Calculate the amount of NaOH required to prepare 250.00 mL of a 1.5 M solution. Weigh it (with a precision of ± 0.1 g) in a beaker, dissolve it in deionized water and let it cool down to room temperature. Transfer the solution quantitatively to a 250.00 mL volumetric flask, dilute it with water, stir it and set the meniscus to the volume mark (remember that the meniscus should be tangent to the mark). This solution must be preserved because it will be used later, in Experiment 10.

3. Standardization of the 1.5 M sodium hydroxide solution.

Take an aliquot of 25.00 mL of the 1.5 M NaOH solution with a pipette and add it to a 250.00 mL volumetric flask, dilute it and set the meniscus to the volume mark. Never put the pipettes in the prepared solutions. Take the necessary volume in a beaker and pipette it from there. Pipettes are calibrated so that the liquid remaining at the tip should not be poured.

This solution will be standardized as follows:

Ask the teaching staff for the preparation of the primary standard ($HOOCC_6H_4COOK$). If necessary, this reagent should be dried at 110 ºC in an oven for three hours to eliminate potential moisture. To prevent further water adsorption onto the reagent, it should be always stored in a desiccator.

Weigh between 0.525 g and 0.637 g of $HOOCC_6H_4COOK$ (with a precision of ± 0.001 g) in a clean 250 mL Erlenmeyer flask. Add 100-150 ml of water and 3-4 drops of an appropriate chemical indicator, such as phenolphthalein.

Take a 25.00 mL burette and fix it with a Fisher clamp (see Figure 1) to a vertical support. Wash the burette three times with a few millilitres of the sodium hydroxide solution, flush it out and finally fill the burette with the solution. Check carefully the absence of air bubbles under

the stopcock. It is strongly recommended that you place a white piece of paper under the Erlenmeyer flask to see the colour changes clearly. As long as the titration is being carried out, the content of the Erlenmeyer flask should be continuously mixed to ensure the homogeneity of the solution (Figure 4).

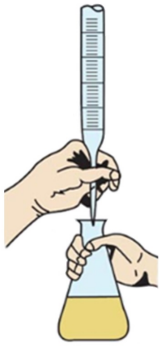


Figure 4. Use of the stopcock and correct position of both hands during titration.

The solution in the burette may be added at a rapid rate at the beginning of the titration and, slowly, drop by drop, when approaching the end point (i.e., near the volume of standard solution at which the analyte has reacted completely). Rinse and drag potential spikes with distilled water from the walls and neck of the Erlenmeyer flask. The titration may be considered finished when the magenta colour of the phenolphthalein persists for at least 30 seconds (Figure 5).

Figure 5. Colour changes of phenolphthalein during acid–base titration of an acid analyte with sodium hydroxide. The middle Erlenmeyer flask shows the optimal colour at the end of the titration.

Once the end point has been reached, measure the pH of the solution with the aid of a pH-meter.

Repeat the entire procedure two more times and write all the results in a table like this:

Titration	**Weigh of standard** (g)	**Volume of NaOH solution** (mL)	**Measured pH**	**Sodium hydroxide concentration** (M)
1	…	…	…	…
2	…	…	…	…
…	…	…	…	…

In addition to the three titrations, a blank essay should be performed, which consists of titration of a mixture of 100-150 mL of water and 3-4 drops of indicator with the sodium hydroxide standard solution. In this way, the potential volume of sodium hydroxide consumed

in the titration of minor acid species in the water or indicator may be subtracted from the volumes of sodium hydroxide measured in the titrations of the primary standard.

For each of the titrations, calculate the exact concentration of the NaOH solution using the volumes of sodium hydroxide and the known masses of $HOOCC_6H_4COOK$. Add the results to the table. From the concentrations calculated for each titration, calculate the average value and the associated error and give the result with the appropriate number of significant figures. From this data, calculate the concentration of the starting sodium hydroxide solution (it should be roughly 1.5 M).

4. Titration of the hydrochloric acid solution prepared in step 1.

Wash a 10.00 mL pipette with 2-3 mL of the *ca.* 1.5 M HCl solution prepared previously. Repeat twice. Do not suck the liquid into the pipette with your mouth: always use an aspirator pear or similar.

Measure 10.00 mL of the hydrochloric acid solution with the pipette and transfer it to a 100.00 mL volumetric flask, dilute it, and set the meniscus to the volume mark.

The diluted HCl solution will be standardized as follows:

Measure 20.00 mL of the diluted hydrochloric acid solution with a pipette and transfer it to a clean Erlenmeyer flask. Add 100-150 mL of water, collecting the drops of solution that may form on the walls. Add 3-4 drops of phenolphthalein solution. Titrate the diluted HCl solution with the standardized sodium hydroxide solution from step 3 until a fair magenta colour is achieved. At this point, measure the volume of standard sodium hydroxide solution added. Measure the pH of the titrated solution with the pH-meter. Repeat the entire procedure two more times and write all the results in a table like this:

Titration	**Volume of HCl solution** (mL)	**Volume of NaOH solution** (mL)	**Measured pH**	**Hydrochloric acid concentration** (M)
1	20.00	…	…	…
2	20.00	…	…	…
…	…	…	…	…

For each one of the titrations, calculate the exact concentration of the hydrochloric acid solution using the volumes of sodium hydroxide and the volumes of hydrochloric acid solution. Add the results to the table. From the concentrations calculated for each titration, calculate the average value and associated error and give the result with the appropriate number of significant figures. From this data, calculate the concentration of the starting hydrochloric acid solution (it should be roughly 1.5 M).

Safety and waste disposal

When using pipettes, always use an appropriate liquid suction device, such as pi-pump or aspirator pears. Never use your mouth!

Carefully insert the pipette into the suction device. Always hold it at the highest part so that it will not break when you insert it into the suction device.

Concentrated hydrochloric acid is corrosive. It may cause burns, and may irritate the respiratory tract, eyes and skin. In case of contact with the eyes, wash off immediately with plenty of water and quickly seek medical assistance.

Sodium hydroxide causes serious burns and irritates the eyes and skin. In case of contact with the eyes, wash off immediately with plenty of water and quickly seek medical assistance.

Dispose of the waste in the designated areas in the lab, as indicated in "*Pla de Gestió de Residus de la Docència Pràctica*" (see page 21).

Questions

1. Consider solid sodium hydroxide, potassium hydrogen phthalate and phenolphthalein. What type of solid do these compounds form? What are the main forces involved in the formation of the solid? Which one do you expect to have the highest melting point?
2. Is the process of dissolving NaOH exothermic or endothermic? Compare it with the dissolution of common salt (NaCl).
3. Imagine that you have a very powerful magnifying glass that allows you to observe the atoms and molecules of a solution. What would you see in the case of the standardized solution of sodium hydroxide? And in the case of the solution of potassium hydrogen phthalate before titration with sodium hydroxide? Draw both images.
4. What error would be made in the titration if air bubbles were present in the burette?
5. Write all the acid–base reactions involved in this experiment.
6. Is there any type of error when deionized water is added to the Erlenmeyer flask during a titration?
7. Why it is necessary to standardize the sodium hydroxide solution?

EXPERIMENT 3 - SYNTHESIS OF NICKEL(II) AND COPPER(II) COORDINATION COMPOUNDS WITH AMINE LIGANDS

Specific objectives

Determination of the limiting reagent and percentage yield.

Vacuum and gravity filtration. Washing of precipitates.

Independent work to be done before starting the experiment

Read the section *Compuestos de coordinación* in Chapter 16 (pages 680-683) of the textbook *Principios de Química. Los caminos del descubrimiento*.

Read the sections *El modelo VSEPR* and *Teoría del enlace de valencia* in Chapter 3 (pages 93-110) of the textbook *Principios de Química. Los caminos del descubrimiento*.

Draw a diagram of the experimental procedure and discuss it with the teaching staff.

Introduction

In this experiment, a series of "coordination compounds" or "complexes" will be prepared. A coordination compound consists of a central atom or ion, which is usually metallic and is called the coordination centre, and a surrounding array of bound molecules or ions, that are known as ligands.

Each ligand should have at least one atom with an electron pair (donor atom), through which the metal–ligand bond is established. Ligands can be classified according to the number of donor atoms they have or the number of positions they occupy around the coordination centre. In this way, NH_3 is a monodentate ligand and ethylenediamine (commonly abbreviated as *en*) is a bidentate ligand.

The number of donor atoms in a complex is denoted as the coordination number (CN). For instance, a complex with 6 NH_3 ligands has a coordination number of 6; in this case, the geometry around the metal ion is octahedral. A complex with 3 *en* ligands also has a CN = 6. Remember that *en* is a bidentate ligand and thus its two nitrogen atoms are attached to the metal, i.e., each *en* ligand occupies two positions of the octahedron. Frequently, the central atom is a metallic ion. Therefore, if the ligands are neutral, the resulting complex will be cationic and it will be found as an ionic compound (a salt), with a cationic complex instead of a simple cation.

The formula of a complex is always written between closed square brackets. The chemical symbol of the metal centre is written first. The ligands are written next. The number of ligands must be indicated by subscript. As an illustrative example, Figure 1 shows the coordination compounds that will be prepared in this experiment.

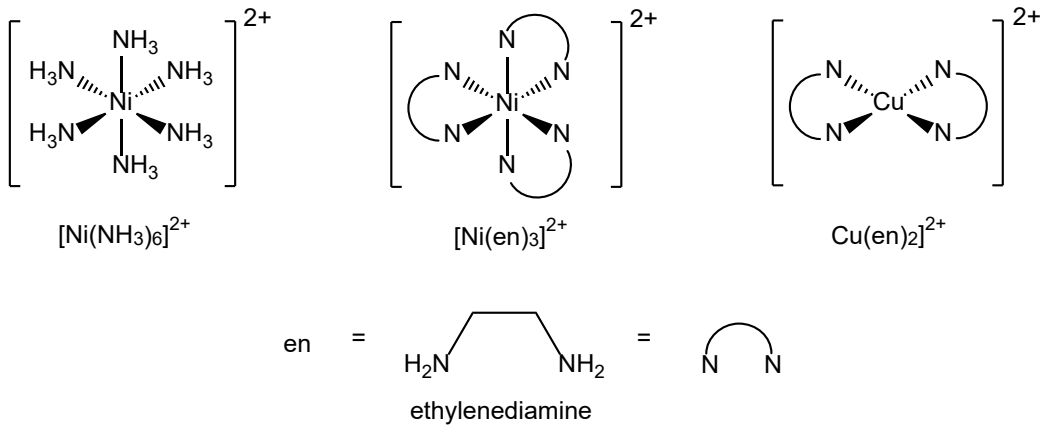


Figure 1. Chemical structure of the coordination compounds that will be prepared in this experiment.

Experimental procedure

$NiCl_{2\,(aq)} + 6\,NH_{3\,(aq)} \rightarrow [Ni(NH_3)_6]Cl_{2\,(s)}$

$NiCl_{2\,(aq)} + Na_2S_2O_{3\,(aq)} + 3\,en_{\,(aq)} \rightarrow [Ni(en)_3]S_2O_{3\,(s)} + 2\,NaCl_{\,(aq)}$

$CuSO_{4\,(aq)} + 2\,en_{\,(aq)} \rightarrow [Cu(en)_2]SO_{4\,(s)}$

All the reactions must be carried out under the fume hood.

1. Preparation of $[Ni(NH_3)_6]Cl_2$.

Dissolve 2 g of $NiCl_2 \cdot 6\,H_2O$ in 4 mL of deionized water in a beaker. Slowly add 8 mL of concentrated ammonia to this solution. Keep the solution in an ice bath for 1 h; a lilac precipitate will appear. Isolate the product by vacuum filtration. Wash the solid with 5 mL of ethanol, air dry it and weigh the product. Calculate the yield of the reaction.

2. Preparation of $[Ni(en)_3]S_2O_3$.

Dissolve 3 g of sodium thiosulphate in 30 mL of deionized water in a beaker. In another beaker, dissolve 3 g of $NiCl_2 \cdot 6\,H_2O$ in 10 mL of deionized water and add 3 mL of ethylenediamine (purity 98%). Warm both solutions and add the thiosulphate solution to the one that contains the $NiCl_2$ and the ethylenediamine. Heat the resulting mixture until it starts boiling. Keep it at this temperature for two minutes. Afterwards, cool the mixture to room temperature. A lilac precipitate will appear. Isolate the product by vacuum filtration. Wash the solid with 15 mL of cold deionized water and air dry it. Dry the product in the oven (at 60 ºC) for 30 minutes. Weigh the product (the sample should be cold) and calculate the yield of the reaction.

3. Preparation of $[Cu(en)_2]SO_4$.

Dissolve 2 g of $CuSO_4 \cdot 5\,H_2O$ in 10 mL of deionized water in a beaker and add 2 mL of ethylenediamine (purity 98%). Add 60 mL of ethanol to the blue solution to induce the precipitation of the product. Place the beaker with the suspension in an ice bath to favour the precipitation. Isolate the dark blue complex by vacuum filtration, wash it with 10 mL of ethanol and air dry it. Weigh the product and calculate the yield of the reaction.

Safety and waste disposal

Ammonia and ethylenediamine are corrosive, avoid breathing their vapours.

$NiCl_2 \cdot 6\ H_2O$ is toxic and $CuSO_4 \cdot 5\ H_2O$ is harmful: avoid contact with eyes and skin.

Dispose of the waste in the designated areas in the lab, as indicated in "*Pla de Gestió de Residus de la Docència Pràctica*" (see page 21).

Questions

1. Draw the Lewis structure of the two ligands (ammonia and ethylenediamine). Indicate the geometry around the central atom and which hybrid orbitals are used to explain the chemical bonds. Can we expect a similar H−N−H bond angle for both compounds? Justify your answer.
2. Justify the greater volatility of ammonia and ethylenediamine than that of nickel(II) chloride and copper(II) sulphate. Is ammonia a gas or a liquid at room temperature? Explain the difference with ethylenediamine. Can we expect a similar melting point for copper(II) sulphate and nickel(II) chloride?
3. Draw the Lewis structure of the thiosulphate and sulphate anions. Indicate the geometry around the central atom. Can we expect a regular geometry (the same distances and angles) around the S atom in the sulphate anion?
4. Explain the function of the ice bath in these syntheses. Is the solubility of these compounds greater or smaller in ethanol than in deionized water?

EXPERIMENT 4 - SYNTHESIS OF ASPIRIN

Specific objectives

Purification of an organic acid.

Vacuum and gravity filtration.

Use of a vacuum desiccator.

Melting point determination.

Thin layer chromatography (TLC).

Independent work to be done before starting the experiment

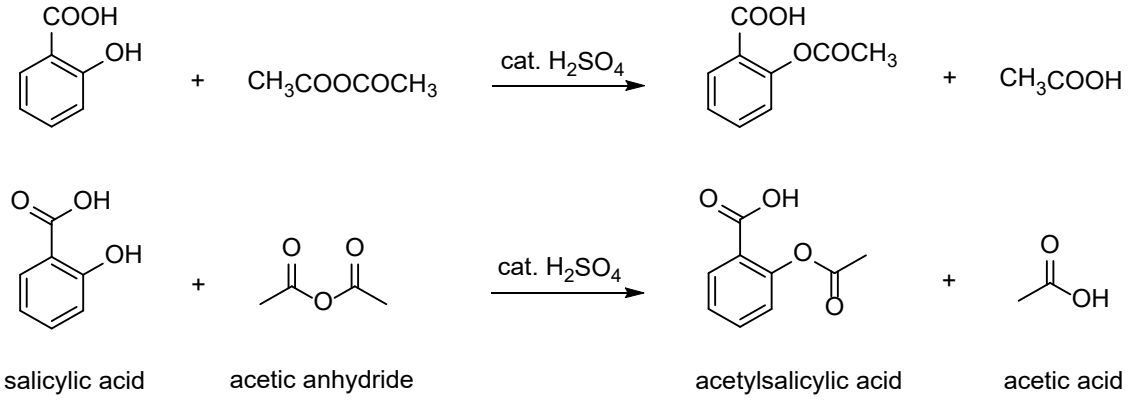
Check the section devoted to chromatography available via the link *Operacions Bàsiques de Laboratori*, in the virtual campus for this course.

Draw a diagram of the experimental procedure and discuss it with the teaching staff.

Introduction

Acetylsalicylic acid (2-ethanoyloxybenzoic acid, pK_a = 3.5), commonly known as aspirin, can be prepared in good yields by esterification of salicylic acid (2-hydroxybenzoic acid, pK_a = 3.0) in an acidic medium. Acetylsalicylic acid is an analgesic: it relieves pain. It also has antipyretic properties, reducing fever.

Experimental procedure



Weigh 2 g of salicylic acid into a clean and dry 100 mL Erlenmeyer flask. Then, 5 mL of acetic anhydride (d = 1.087 g/mL) is added, followed by 5 drops of concentrated sulphuric acid (96% w/w). The mixture is stirred until the acid dissolves completely and is gently heated in a steam bath at 80 ºC for 15 min. The flask is then left to cool down to room temperature and the solution is further cooled to 0 ºC by placing the flask in an ice/water bath. At this point, crystals begin to precipitate. If no crystals are observed, their formation can be favoured by carefully scratching the inside walls of the Erlenmeyer flask using a glass rod. 50 mL of water is then added, and the reaction mixture is stirred for two minutes and left standing, at 0 ºC, until the crystallization process is complete. The solid formed is filtered using a Büchner funnel, washed with cold water and air dried for 10 min (still in the Büchner funnel and connected to the water

aspirator or vacuum pump). Dry a small amount of product (spatula tip) by spreading it over a small piece of porous plate and determine its melting point. Also, set aside a small aliquot of product to perform a TLC analysis at the end of the experiment.

The product is purified as follows: the solid to be purified is transferred to a 100 mL beaker and 25 mL of a saturated solution of sodium hydrogencarbonate is slowly added until CO_2 evolution is no longer observed (the slow addition of sodium hydrogencarbonate is necessary because strong effervescence occurs). Check that the final solution is basic and then filter it through a fluted filter paper. The filtrate is then poured slowly into a solution of 3.5 mL of concentrated HCl in 10 mL of water, with occasional stirring. Check that the pH of the solution is now acid. The mixture is cooled in an ice/water bath and the solid that forms is filtered using a Büchner funnel, washed with water at 0 ºC and dried, first using filter paper to absorb most of the water, and then left in a vacuum desiccator with P_2O_5 or anhydrous $CaSO_4$ as a drying agent. The teaching staff will show you how a desiccator works, how to create and release the vacuum inside and how to check if the drying agent is in perfect condition or should be renewed. Once the solid is dry, determine its melting point and calculate the yield of the reaction.

The purity of the product can be checked using the reaction of iron(III) chloride with phenols (such as salicylic acid). Formation of an iron–phenol complex with iron(III) generates a purple coloration. This test can be performed using three test tubes containing a spatula tip of the acetylsalicylic acid prepared, before and after purification, and salicylic acid respectively. Next, 5 mL of water and 5-6 drops of a 1% iron(III) chloride solution are added to each tube.

Also evaluate the purity of your product by TLC, using dichloromethane/ethyl acetate 3:1 (v/v) as the eluent. Include in your TLC the product you obtained before and after purification and use the salicylic acid and acetylsalicylic acid standards available in the lab.

Safety and waste disposal

Concentrated sulphuric acid is corrosive and causes serious burns. In case of skin contact, immediately flush the affected area with abundant water.

Phosphorus pentoxide is a strong dehydrating agent. It is corrosive and causes serious burns. In case of skin contact, immediately wash the affected area with abundant water.

Dispose of the waste in the designated areas in the lab, as indicated in "*Pla de Gestió de Residus de la Docència Pràctica*" (see page 21).

Questions

1. Once the reactants for the synthesis of aspirin have been added, why is it necessary to stir until dissolution is complete?
2. Filtration using a Büchner funnel is used to separate acetylsalicylic acid from the reaction medium. Could a conical funnel be employed instead? Which of the two types of funnel is the right one for this particular filtration and why?
3. Why is the melting point a criterion for purity?
4. To purify acetylsalicylic acid, it is treated with a saturated sodium hydrogencarbonate solution first and then with a HCl solution. Explain the phenomena observed.
5. Name several drying agents commonly used in a desiccator.

6. Why is the melting point of aspirin lower than that of salicylic acid?
7. Draw the complete Lewis structure of acetic anhydride and indicate the hybridization of its carbon atoms. What is the value of the O–C–O angle?

EXPERIMENT 5 - SEPARATION OF LIQUID MIXTURES BY DISTILLATION

Specific objectives

Separation of the components of a liquid mixture by simple and fractional distillation.

Introduction

Distillation is one of the most common techniques for purifying liquids. The components of a mixture can be separated by ***simple distillation*** if they have significantly different boiling points (greater than 100 ºC). In a simple distillation, the liquid mixture is boiled in a round-bottom flask (distilling flask) and the vapours are conducted to a cool surface (condenser) where they condense again. The condensed vapours (distillate) drip into a reservoir separated from the original mixture (receiving flask). If the components of the mixture have more similar boiling points, ***fractional distillation*** can be used to improve separation. In fractional distillation, glass beads in a fractionating column (or Vigreux column) are used to obtain vapours enriched in the most volatile component. Vapours from the boiling mixture reflux in the fractionating column (condense and drip back to the distilling flask again) until the temperature at the top of the fractionating column is high enough for the most volatile compound to escape and enter into the condenser.

Experimental procedure

All glass material required as distillation apparatus must be clean and dry.

1. Simple distillation.

Prepare a mixture containing 55 mL of glacial acetic acid and 20 mL of acetone. Pour the mixture into a 100 mL round-bottom flask and add some boiling chips. Assemble the simple distillation apparatus as depicted in Figure 1 and secure the setup with clips and clamps.

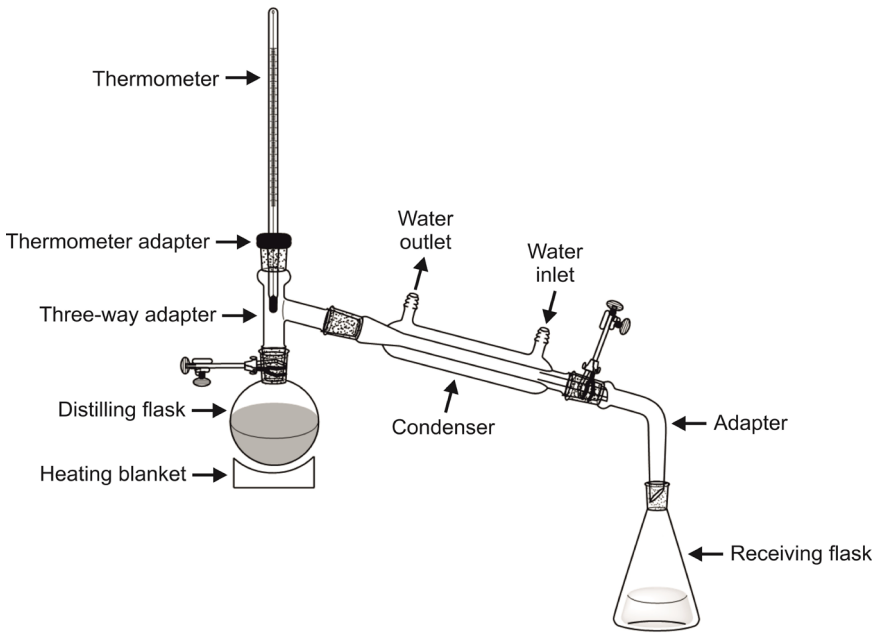


Figure 1. Simple distillation apparatus.

Connect the water cooling circuit and start heating. Control the rate of heating in order to collect a drop of distillate per second (approximately). Collect 1 mL fractions in test tubes (10-15 tubes) and write down the temperature of each fraction. Add one drop of methyl red to each test tube and write down the observed colour.

2. Fractional distillation.

Prepare a mixture containing 55 mL of glacial acetic acid and 20 mL of acetone. As in the previous section, assemble the fractional distillation setup as depicted in Figure 2 and secure all the pieces with clips and clamps.

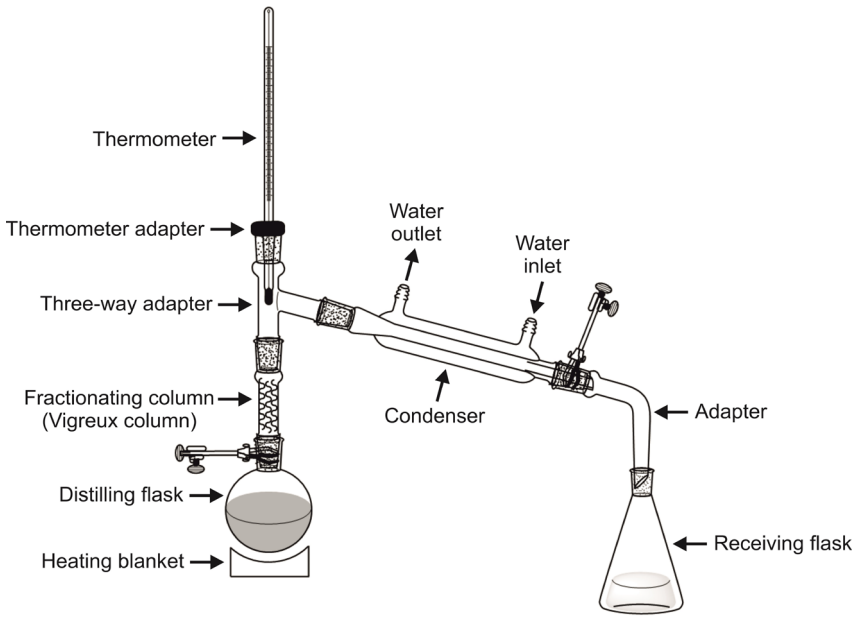


Figure 2. Fractional distillation apparatus.

Control the rate of heating to obtain one drop per second of distillate (ideally use the same heating blanket as for the simple distillation). Collect 1 mL fractions in test tubes (10-15 tubes) and add one drop of methyl red to each tube. Compare the distillation temperatures of the fractions and the resulting colour with those obtained for simple distillation.

Safety and waste disposal

Glacial acetic acid is corrosive, flammable and causes severe burning.

Acetone is flammable (F).

Dispose of the waste in the designated areas in the lab, as indicated in "*Pla de Gestió de Residus de la Docència Pràctica*" (see page 22).

Questions

1. Justify the temperature of the fractions obtained with both types of distillation.
2. How is reflux formed in the fractionating column? How does the length of the Vigreux column influence the efficiency of fractional distillation?
3. Explain why the water cooling circuit must be connected as depicted in Figures 1 and 2.

EXPERIMENT 6 - EXTRACTION OF CAFFEINE FROM SOFT DRINKS

Specific objectives

Liquid–liquid extraction.

Use of the rotary evaporator.

Thin layer chromatography (TLC).

Independent work to be done before starting the experiment

Check the section devoted to chromatography accessible via the link *Operacions Bàsiques de Laboratori*, in the virtual campus for this course.

Draw a diagram of the experimental procedure and discuss it with the teaching staff.

Introduction

The kola nut is the fruit of the kola tree, a genus (Cola) of trees that are native to the tropical rainforests of Africa. The caffeine-containing fruit of the tree is used as a flavouring ingredient in beverages, and is the origin of the term "cola". In this experiment, we will extract and isolate the caffeine (Figure 1) present in a cola drink and quantify the amount of this organic compound normally found in this kind of beverages.

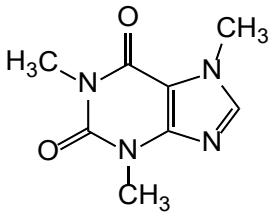


Figure 1. Chemical structure of caffeine.

There are several extraction techniques, for instance, solid–liquid extraction and liquid–liquid extraction. The latter, used in this experiment, involves transferring a compound dissolved in a determined solvent to another where it is significantly more soluble. The ratio of concentrations of such a substance in a mixture of two immiscible solvents at equilibrium is constant and it is given by the partition or distribution coefficient, k ($k = c_1/c_2$), where c_1 and c_2 are the concentrations of the compound dissolved in each solvent.

Experimental procedure

Place 320 mL of cola drink in a beaker and stir the content with a glass rod in order to remove as much gas as possible. Half the volume (~160 mL) is then transferred to a 250 mL separatory funnel and extracted with 25 mL of methylene chloride (dichloromethane). The mixture is stirred, first carefully and later more vigorously, and left to settle until the two phases separate. Be careful with the gas that is generated! The pressure that builds up inside the funnel must be released from time to time. When you vent the funnel, point the stem of the funnel away from everybody, so that the solvent and gases that are released are not blown into anybody's face. The organic layer is separated from the aqueous one by opening the stopcock of the separatory funnel. The separatory funnel should be opened (not closed with the stopper)

when separating the organic and the aqueous layer. This procedure is repeated twice more. All the organic phases, which contain the caffeine, are collected in the same Erlenmeyer flask. The other half of the cola drink is placed in the separatory funnel and the previous procedure is repeated. The combined organic extract is transferred to the separatory funnel and washed with 10 mL of a saturated $NaHCO_3$ solution in order to eliminate variable amounts of benzoic acid that the soft drink might contain as an additive. The combined organic extract is dried over anhydrous Na_2SO_4 (the drying agent). Solid anhydrous Na_2SO_4 should be added until you notice that the fresh drying agent does not cling to other particles or to the glass wall when swirling the solution. Afterwards, the flask is closed with a stopper and left for 10 minutes with occasional manual stirring. The drying agent is separated by filtration using a fluted filter paper and a conical funnel, and the filtrate is collected in a clean and dry round-bottom flask. The filtrate is concentrated in a rotary evaporator to a volume of 2–3 mL. The remaining solution is transferred, with a dropper, to a pre-weighed 10 mL round-bottom flask and the solvent is removed under reduced pressure without heating the flask with the external bath.

Determine the amount of caffeine recovered.

Check the purity of the caffeine isolated by thin layer chromatography (TLC). Use ethyl acetate as the eluent (mobile phase).

Safety and waste disposal

Be careful with the separatory funnel during the extractions. Generally, a gas is generated inside the separatory funnel and can cause it to open unexpectedly, explosively! In order to avoid this, shake the separatory funnel very gently at the beginning of the extractions. A simple rotatory movement will be enough.

Methylene chloride (dichloromethane) is harmful. Avoid contact with the skin.

Dispose of the waste in the designated areas in the lab, as indicated in "*Pla de Gestió de Residus de la Docència Pràctica*" (see page 22).

Questions

1. Why is Na_2SO_4 filtered through fluted filter paper in a conical funnel instead of using a Büchner funnel?
2. Comment on the difference in the performance of the extraction process if instead of making three consecutive extractions with portions of 25 mL, only one single extraction with 75 mL of dichloromethane is made.
3. Draw the Lewis structure of caffeine.

EXPERIMENT 7 - REACTION UNDER REFLUX: SYNTHESIS OF ISOAMYL ACETATE (BANANA OIL)

Specific Objectives

Run a reaction under reflux.

Liquid–liquid extraction.

Use of the rotary evaporator.

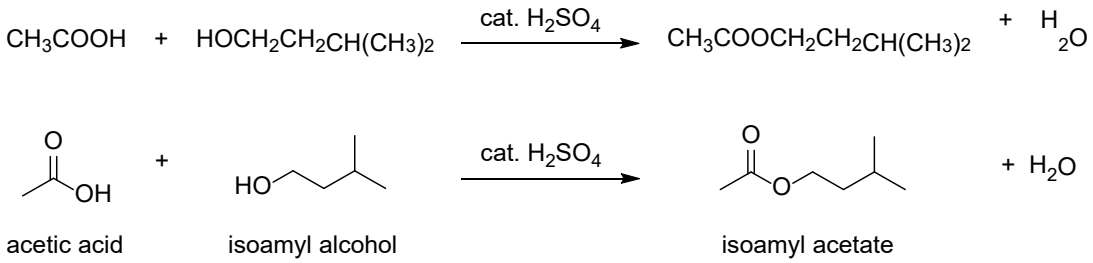
Independent work to be done before starting the experiment

Draw a diagram of the experimental procedure and discuss it with the teaching staff.

Introduction

The aim of this experiment is the preparation of an ester by an esterification procedure known as the *Fischer reaction*. Present wild in nature, the smallest and most volatile esters commonly smell good. The ester you will synthesize here smells like banana oil and acts as an alarm pheromone for honeybees. Pheromones are substances that living beings use for chemical communication. When a bee stings someone, in addition to injecting poison, it also segregates a small amount of the alarm pheromone. Thus, worker bees are prompted to attack the intruder when they detect the pheromone.

Experimental procedure



All glassware should be cleaned and dried before use to prevent yield loss.

To a 100 mL round-bottom flask, add 18 mL (14.6 g) of 3-methyl-1-butanol (isopentanol or isoamyl alcohol) and 23 mL (24 g) of glacial acetic acid (both measured with a measuring cylinder). Then, very carefully add 0.5 mL (2-3 drops) of concentrated H_2SO_4, shake the flask gently and add some boiling chips.

Assemble the reflux setup as depicted in Figure 1 and fix it with only one clamp placed on the neck of the flask.

The reaction mixture is heated under reflux for 1 hour.

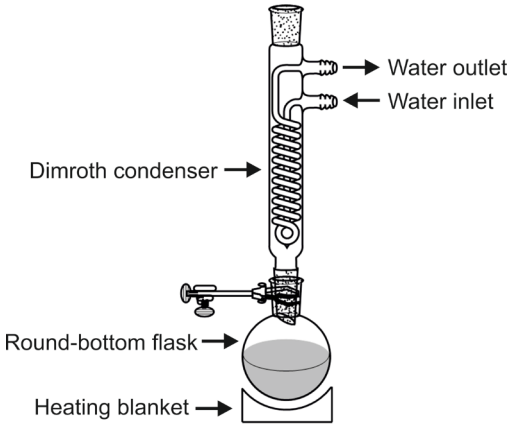


Figure 1. Reflux apparatus.

After cooling down the reaction to room temperature, pour the mixture into a 250 mL separating funnel, dilute the contents by adding 25 mL of CH_2Cl_2 and add, little by little, 50 mL of cold water (previously cooled in an ice bath). Stopper the separating funnel, gently swirl the phases to prevent excess pressure being generated by the release of carbon dioxide and decant the organic layer. The organic layer can be easily identified by adding a drop of water and looking to see which layer it dissolves in; the drop will dissolve in the aqueous layer. Once the organic layer is separated from the aqueous one, wash the organic layer with 50 mL of $NaHCO_3$ solution in order to eliminate traces of acetic acid. Double check that the aqueous layer is still basic. Wash the organic layer again with an additional 50 mL of water. If an interface forms, it can be eliminated by adding saturated NaCl; the two layers should be perfectly separated. Decant and dry the organic phase with anhydrous Na_2SO_4. Solid anhydrous Na_2SO_4 should be added until you notice that the fresh drying agent does not cling to other particles or to the glass wall when swirling the solution. Afterwards, the flask is closed with a stopper and left for 10 minutes with occasional manual stirring. Filter the organic phase through fluted filter paper, transfer the resulting filtrate to a 100 mL round-bottom flask, previously tared, and evaporate the solvent in the rotary evaporator until an oil is obtained. Weigh the product obtained and calculate the yield of the reaction.

Safety and waste disposal

Glacial acetic acid is corrosive, flammable and produces severe burns.

Sulphuric acid is corrosive and produces severe burns. In case of contact with the skin, rinse immediately with plenty of water.

3-Methyl-1-butanol is flammable and nocive by inhalation. Prevent contact with eyes and skin.

Dispose of the waste in the designated areas in the lab, as indicated in "*Pla de Gestió de Residus de la Docència Pràctica*" (see page 22).

Questions

1. Why is the organic layer washed with water after being washed with $NaHCO_3$?
2. Explain why the addition of sodium chloride helps to destroy an interface.
3. Enumerate the steps to follow when using a rotary evaporator.
4. Why should boiling chips be added to the reaction flask?

EXPERIMENT 8 - ABSORPTION SPECTRA. USE OF A SPECTROPHOTOMETER TO ASSESS THE LAMBERT-BEER LAW

Specific objectives

Preparation of solutions. Use of volumetric equipment.

Use of a spectrophotometer to record absorption spectra.

Assessment of the Lambert-Beer law (linear relationship between absorbance, A, and concentration, c).

Interpolation: use of the linear A-c dependence to determine the concentration of a chemical species in a solution.

Independent work to be done before starting the experiment

Read the sections *Características de la radiación electromagnética* in Chapter 1 (pages 3 and 4) and *Espectroscopía visible y ultravioleta* in Chapter 3 (pages 130 and 131) of the textbook *Principios de Química. Los caminos del descubrimiento*.

Draw a diagram of the experimental procedure and discuss it with the teaching staff.

Introduction

Light of a specific wavelength (λ) possesses a determinate energy ($E = h \cdot c / \lambda$, where h and c are Planck's constant and the speed of light, respectively). When light travels through a solution containing absorbing molecules, this energy can be absorbed by some of their electrons, which are promoted to higher energy levels. As a result, the intensity of the light beam that comes out of the sample is less than that of the incident beam (notice the different colour of the two green light beams in Figure 1). This phenomenon is called light absorption.

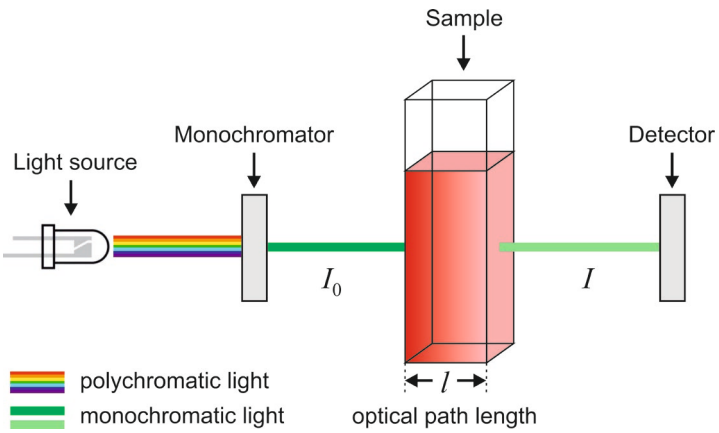


Figure 1. Light absorption and spectrophotometric measurement.

Light absorption can be measured experimentally with a spectrophotometer. Briefly, this instrument has a light source, a monochromator and a detector (Figure 1). The light source emits polychromatic light. This light is directed to the monochromator where a single wavelength is selected. The monochromatic radiation thus generated then passes through the sample and part of it is absorbed. Finally, the detector measures the amount of light that has passed through the solution, i.e., the light that has not been absorbed by the molecules.

A spectrophotometer may display either transmittance or absorbance values. Transmittance (T) quantifies the amount of light that has passed through the solution, i.e., the non-absorbed light. Indeed, transmittance is defined as the ratio between the light intensity before (I_0) and after (I) the beam interacts with the sample. Transmittance is thus calculated by equation (1):

$$T = \frac{I}{I_0} \tag{1}$$

On the other hand, absorbance (A) refers to the amount of light absorbed by the solution. The relationship between T and A is given by equation (2):

$$A = -log_{10}T \tag{2}$$

The use of absorbance is generally preferred since this magnitude can be directly related with the concentration of the absorbing species in the sample (c, which can be expressed either in mol L^{-1} or in mass units L^{-1}). The relationship between A and c is described by the well-known Lambert-Beer law (equation (3)):

$$A = \varepsilon_\lambda \cdot l \cdot c \tag{3}$$

where l is the optical path length (i.e., the distance that the light travels through the solution, see Figure 1) and ε_λ is a proportionality constant, which has a different value for each wavelength and chemical compound. When the concentration of the absorbing species is expressed in mol L^{-1}, ε_λ is called the molar absorption coefficient (L mol^{-1} cm^{-1}).

Experimental procedure

1. Measurement of the absorption spectrum of a potassium permanganate solution.

Prepare a 20 mg L^{-1} potassium permanganate solution by diluting the 200 mg L^{-1} stock solution available in the laboratory.

The absorption spectrum of the diluted potassium permanganate solution prepared will be registered with a *Spectronic 20* spectrophotometer. Figure 2 shows the basic operation of the instrument. For further details, read the standard operating protocol (SOP) available in the laboratory.

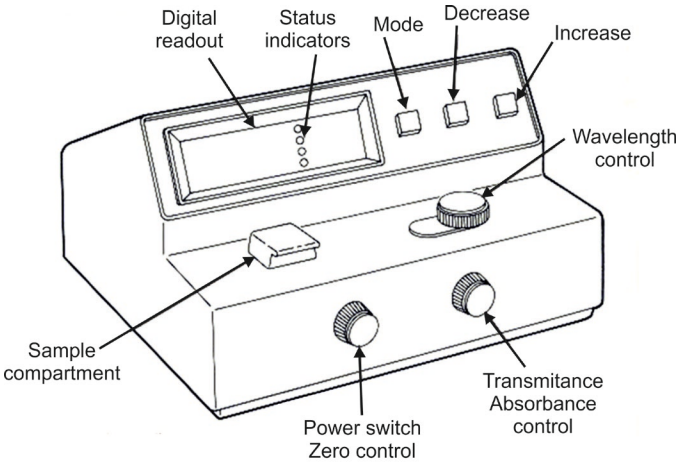


Figure 2. Spectrophotometer *Spectronic 20*.

Calibrate the spectrophotometer following the instructions. To record the spectrum of the diluted potassium permanganate solution that you have prepared, half fill the cuvette with this solution. Measure %T and A of the solution between 400 nm and 600 nm (record %T and A values every 20 nm). Note that you must calibrate the instrument every time you change the wavelength. Make a graph of A versus wavelength (absorption spectrum) and another of %T versus wavelength.

2. Experimental assessment of the Lambert-Beer law.

To experimentally evaluate compliance to the Lambert-Beer law, you will need to prepare a series of $KMnO_4$ solutions of different but precisely known concentrations (named standard solutions). These solutions must be prepared using volumetric equipment, such as volumetric flasks and bulb pipettes.

Prepare four $KMnO_4$ standard solutions by taking 2, 5, 10, and 25 mL of the 200 mg L^{-1} stock solution, pouring them into 100.00 mL volumetric flasks and making them up to the mark with deionized water (use a dropper to add the last drops). Cover the volumetric flasks with stoppers and homogenize the solutions by shaking.

In according with the absorption spectrum recorded previously, find the wavelength of maximum absorption. Calibrate the spectrophotometer at this wavelength, as described in the SOP of the spectrophotometer, and measure the absorbance of the four standard solutions (start measuring the most diluted solution and finish with the most concentrated one). Before each measurement, wash the cuvette three times with the next solution.

Use a spreadsheet (e.g., Microsoft Excel) to make a graph of absorbance versus concentration. Check the linear relationship between absorbance and concentration. Is there any anomalous point? If so, ask the teaching staff about it. Use the spreadsheet to calculate the equation of the line and determine the value of the absorption coefficient, ε.

3. Determination of the permanganate concentration of an unknown sample.

Ask the teaching staff for a potassium permanganate solution whose concentration you will determine. Measure the absorbance value of the solution following the protocol described in the previous section. Find the permanganate concentration of the problem solution by interpolating the measured absorbance value in the graph or by introducing it into the equation of the line.

Safety and waste disposal

When using pipettes, always use an appropriate liquid suction device, such as pi-pump or aspirator pears. Never use your mouth!

Carefully insert the pipette into the suction device. Always hold it at the highest part so that it will not break when you insert it into the suction device.

Potassium permanganate is harmful by ingestion. It is a strong oxidizer. Contact with liquid combustible materials may result in spontaneous ignition.

Dispose of the waste in the designated areas in the lab, as indicated in "*Pla de Gestió de Residus de la Docència Pràctica*" (see page 22).

Questions

1. What is the relation between the colour corresponding to the wavelength range of maximum absorption of permanganate and the colour that is observed in solution?
2. Could the linear relationship between absorbance and concentration be checked at any wavelength of the spectrum? What differences would you expect to find?
3. Why do we use volumetric flasks and bulk pipettes to prepare the standard solutions?

EXPERIMENT 9 - STANDARDIZATION OF A PERMANGANATE SOLUTION BY MEANS OF A REDOX TITRATION

Specific objectives

Standardization of a permanganate solution by means of a redox titration using sodium oxalate as a primary standard.

Independent work to be done before starting the experiment

Read Section L.3 (*Análisis volumétrico*) in the chapter *Fundamentos* (pages F89-F92) of the textbook *Principios de Química. Los caminos del descubrimiento*.

Draw a diagram of the experimental procedure and discuss it with the teaching staff.

Introduction

Redox volumetry is based on a procedure similar to that developed in an acid–base titration (see Experiment 2 above). In this instance, however, the concentration of a reducing agent (which is oxidized) will be calculated, by knowing the concentration of an oxidizing agent (which is reduced) or vice versa.

Experimental procedure

1. Preparation of a *ca.* 0.02 M potassium permanganate solution.

Weigh in a beaker the appropriate amount of potassium permanganate to prepare 100 mL of a 0.02 M solution. Dissolve it in deionized water and, once the entire solid is dissolved, transfer the solution quantitatively to a 100.00 mL volumetric flask and set the meniscus to the volume mark with deionized water.

2. Redox titration with sodium oxalate.

Dry the sodium oxalate at 105 ºC in an oven for two hours and then store it in the desiccator (ask the teaching staff). Weigh between 0.120 and 0.140 g of sodium oxalate (with a precision of ± 0.001 g) and place it in a 250 mL clean and well-dried Erlenmeyer flask. Add about 35 mL of deionized water. You will see that it does not dissolve completely. Add about 20 mL of 4 M sulphuric acid (it is already prepared in the laboratory) and heat the solution in a water bath at 60 ºC until the oxalate has dissolved completely (about ten minutes).

Fix a 25.00 mL burette to a vertical support with a Fisher clamp (see Figure 1 on page 34). Wash it three times with a few millilitres of the 0.02 M $KMnO_4$ solution. Flush it out and finally make the burette up to volume with this solution (check carefully that there are no air bubbles under the stopcock or in the column). As long as the titration is being carried out, the Erlenmeyer flask (still hot) must be continuously mixed. The solution in the burette is added at a rapid rate at the beginning of the titration and then slowly, drop by drop, when approaching the end point. The titration ends when the Erlenmeyer solution turns a slightly pink colour due to an excess of permanganate.

Repeat the entire procedure twice more and write all the results in a table like this:

Titration	**Weigh of sodium oxalate** (g)	**Volume of $KMnO_4$ solution** (mL)	**$KMnO_4$ concentration** (M)
1	…	…	…
2	…	…	…
…	…	…	…

Determine the exact concentration of the permanganate solution you have prepared.

Safety and waste disposal

Concentrated sulphuric acid is corrosive and causes serious burns. In case of skin contact, immediately rinse the affected area with abundant water.

Potassium permanganate is harmful by ingestion. It is a strong oxidizer. Contact with liquid combustible materials may result in spontaneous ignition.

Dispose of the waste in the designated areas in the lab, as indicated in "*Pla de Gestió de Residus de la Docència Pràctica*" (see page 23).

Questions

1. Write out the reactions that take place in the titration of potassium permanganate with sodium oxalate.
2. Justify why the titration starts with the oxalate solution warmed.
3. Justify the rapid addition of potassium permanganate at the beginning of the titration.
4. Is it necessary to add an indicator in this titration? Why/Why not?
5. Briefly describe some possible applications for this type of redox titrations.

EXPERIMENT 10 - ENTHALPY OF A NEUTRALIZATION REACTION

Specific objectives

Determination of the heat of neutralization for a reaction.

Use of a calorimeter.

Independent work to be done before starting the experiment

Read Sections 7.5, 7.6, 7.9, 7.13 and 7.14 in Chapter 7 (pages 243-251, 254-255 and 261-264) of the textbook *Principios de Química. Los caminos del descubrimiento*.

Draw a diagram of the experimental procedure and discuss it with the teaching staff.

Introduction

The heat exchanged in any given physicochemical process can be determined by using a calorimeter (also called a *Dewar flask*, Figure 1).

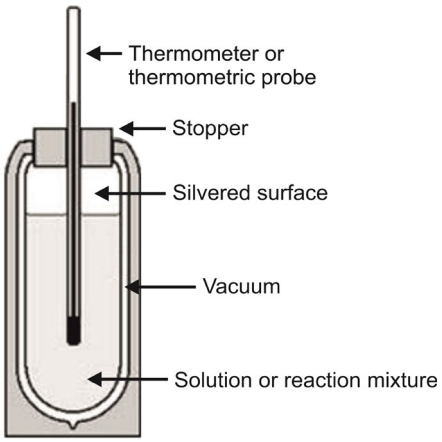


Figure 1. Schematic representation of a calorimeter or Dewar flask.

A calorimeter is a closed adiabatic container, i.e., it does not allow any thermal energy exchange (heat transfer) between the inner system and the outer environment. If the process under study occurs at constant pressure (atmospheric pressure in the laboratory), then $q_P = \Delta H = 0$. Therefore, if the reaction inside the calorimeter is exothermic, the heat released causes the heating of the system, whereas for an endothermic reaction the system cools down. Considering an adiabatic transformation at constant pressure, the following relation (equation (1)) is fulfilled:

$$\Delta H = \Delta H_{\text{reaction}} + \Delta H_{\text{heating/cooling}} = 0 \qquad (1)$$

where $\Delta H_{\text{reaction}}$ is the heat released or absorbed at constant pressure during the reaction, and $\Delta H_{\text{heating/cooling}}$ is the heat related to the heating or cooling of the inner system. The latter term can be determined experimentally by measuring the mass of all the components of the whole system and the temperature variation, according to equation (2):

$$\Delta H_{\text{heating/cooling}} = \sum_i m_i \, c_{e,i} \, (T_2 - T_1) \qquad (2)$$

where $c_{e,i}$ is the specific heat, whose value can be considered that of water (i.e., 1 cal g^{-1} $ºC^{-1}$) when dealing with aqueous solutions.

Since the walls of the calorimeter also play a role during heat transfer, it is necessary to take into account the amount of heat absorbed or released by the container in each trial. The influence of the calorimeter on the process is represented by the so-called *water equivalent of the calorimeter* (m_c), which is defined as the mass of water that would absorb or lose the same quantity of heat as the calorimeter that is in contact with the solution. Hence, before undertaking a calorimetry experiment, the calorimeter that is going to be employed must be calibrated, thus obtaining the corresponding m_c value. This value, along with the total mass of solution, can then be introduced into the $\Sigma_i m_i$ term in order to calculate $\Delta H_{\text{heating/cooling}}$.

Once $\Delta H_{\text{heating/cooling}}$ has been determined, the heat exchanged during the reaction can be calculated as:

$$\Delta H_{\text{reaction}} = -\Delta H_{\text{heating/cooling}} \qquad (3)$$

The aim of this experiment is to determine the enthalpy of the following neutralization reaction:

$$H_3O^+ + OH^- \rightarrow 2\,H_2O$$

using the hydrochloric acid (~1.5 M) and sodium hydroxide (~1.5 M) solutions prepared and standardized previously in Experiment 2.

Experimental procedure

The calorimeter, empty and closed, is weighed (always with the rubber stopper in place and without the temperature probe). Based on the concentrations of the HCl and NaOH solutions, prepared and standardized previously in Experiment 2, calculate the volume of NaOH solution needed to neutralize 50 mL of the HCl solution. Measure this volume in a graduated cylinder and add about 5 mL in excess. Introduce this solution into the calorimeter, add 2-3 drops of phenolphthalein, close the container with the rubber stopper and measure the solution temperature with the probe (ensure that the value is stable). Take out the probe and weigh the calorimeter as explained above. Then, add 50 mL of the HCl solution (measured in a graduated cylinder). Rapidly close the calorimeter with the stopper, introduce the probe, shake vigorously and write down the temperature reached upon stabilization. Take out the probe and weigh the calorimeter as explained above. Once the trial has been finished, verify that the solution is pink, which provides information on the progress of the neutralization reaction.

Repeat the entire procedure two times more and write all the results in a table like this:

Exp.	**Mass of the calorimeter** (g)	**Mass of NaOH solution** (g)	T_1 (ºC)	T_2 (ºC)	**Total mass of solution** (g)	**Mass of HCl solution** (g)	$\Delta H_{\text{reaction}}$ (cal)
1	…	…	…	…	…	…	
2	…	…	…	…	…	…	
3	…	…	…	…	…	…	

For the calorimeters that are available in the laboratory, m_c is 15 g if the total solution volume is around 100-120 mL.

Application of equations (2) and (3) for the neutralization reaction allows us to determine the heat of reaction at constant pressure (equation (4)):

$$\Delta H_{\text{reaction}} = -(m_{\text{NaOH}} + m_{\text{HCl}} + m_c)\, c_{e,i}\, (T_2 - T_1) \qquad (4)$$

In each trial, calculate the number of moles of HCl that are neutralized (n_{HCl}), based on the solution concentration, and the mass, considering that the density is 1 g cm^{-3}. Provide the value of the heat of neutralization per mole of acid for each single trial, and then calculate the average value from three valid trials. The heat of neutralization per mole of acid can be calculated as:

$$\Delta H_{\text{neutralization}} = \frac{\Delta H_{\text{reaction}}}{n_{\text{HCl}}} \qquad (5)$$

Summarize the results of your calculations in a table like this:

Exp.	$\Delta H_{\text{reaction}}$ (cal)	n_{HCl} (mol)	$\Delta H_{\text{neutralization}}$ (cal)
1	…	…	…
2	…	…	…
3	…	…	…

Safety and waste disposal

Concentrated hydrochloric acid is corrosive. It may cause burns, and may irritate the respiratory tract, eyes and skin. In case of contact with the eyes, wash off immediately with plenty of water and quickly seek medical assistance.

Sodium hydroxide causes serious burns and irritates the eyes and skin. In case of contact with the eyes, wash off immediately with plenty of water and quickly seek medical assistance.

Dispose of the waste in the designated areas in the lab, as indicated in "*Pla de Gestió de Residus de la Docència Pràctica*" (see page 23).

Questions

1. Is the neutralization reaction between HCl and NaOH an exothermic or endothermic process?
2. Is the neutralization reaction a slow or quick process?
3. Why is it necessary to consider the water equivalent of the calorimeter?
4. Why must the total solution volume inside the calorimeter in each trial be around 100-120 mL?
5. Compare the average value obtained for the heat of neutralization per mole of acid with the tabulated one. What are the possible causes of the difference observed?
6. Would the heat of neutralization change if:
    a) instead of neutralizing 1.5 M HCl, a 10 M HCl solution had been used?
    b) another strong acid like HNO_3 had been neutralized instead of HCl?
    c) a weak acid like acetic acid had been neutralized instead of HCl?

EXPERIMENT 11 - ELECTROCHEMICAL CELLS: PROCESSES AND ELECTROMOTIVE FORCE

Specific objectives

Identify the elements of an electrochemical cell.

Understand how electrochemical cells work.

Produce the appropriate electrochemical cell notation.

Measure the electromotive force (EMF) of an electrochemical cell.

Comprehend the relation between EMF and the electroactive species concentration.

Independent work to be done before starting the experiment

Read Sections 13.3, 13.4, 13.5, 13.6 and 13.9 in Chapter 13 (pages 522-534 and 538-541) of the textbook *Principios de Química. Los caminos del descubrimiento*.

Draw a diagram of the experimental procedure and discuss it with the teaching staff.

Introduction

When an electronic conductor (in this case a metal) is placed in contact with an ionic conductor (in this case an electrolyte solution) we have an *electrode*. The system formed by the combination of two electrodes, so that the two ionic conductors come into contact, constitutes an electrochemical or galvanic cell (*pila* in Catalan). The two electrolyte solutions can come into direct contact or it can be via a salt bridge.

In a galvanic cell, an electron transfer process occurs simultaneously at both electrodes. The electrode where the oxidation reaction takes place, for instance $a\,\mathrm{A} \rightarrow b\,\mathrm{B} + n\,\mathrm{e}^-$, is called the *anode* (the negative pole). Meanwhile, the reduction reaction, e.g., $c\,\mathrm{C} + n\,\mathrm{e}^- \rightarrow d\,\mathrm{D}$, happens at the *cathode* (the positive pole). Thus, the equation of the global chemical reaction is:

$$a\,\mathrm{A} + c\,\mathrm{C} \;\Leftrightarrow\; b\,\mathrm{B} + d\,\mathrm{D}$$

This spontaneous chemical reaction, however, only takes place when electrical contact is established between the two electronic conductors (in this case the metals), i.e., when there is a potential difference between the electrodes. Under these conditions, the reaction progresses with an electric current flowing through the external circuit. As a result, the chemical energy released by the spontaneous chemical reaction is converted into electrical energy. It should be noted that the cell voltage will diminish over time as the reaction proceeds.

There are many possible galvanic cells, so a shorthand notation is usually used to describe them. The cell notation (sometimes called a cell diagram) provides information about the various species involved in the reaction. In the case of our example, the cell notation would be:

$$(-)\;\mathrm{A}\,|\,\mathrm{B}\;\|\,\mathrm{C}\,|\,\mathrm{D}\;(+)$$

by convention, the anode is placed on the left and the cathode is placed on the right. Vertical bars separate the different phases and the double vertical line denotes an interface separated by a salt bridge. If there is no salt bridge connecting the two electrodes, the double vertical line (||) is

replaced by a vertical bar (|). When the half-reaction includes more than one species in the same phase, they are separated by commas (X_1, X_2, ...), and the inert metal that acts as a metallic conductor is separated by a single vertical bar. This inert metal (M) is usually graphite or a noble metal. Then the notation of this half-reaction would have the form M | X_1, X_2 ...

In a galvanic cell, the electromotive force (EMF, *força electromotriu* (*FEM*) in Catalan) is the voltage difference between its two electrodes when current does not flow, that is, when the chemical reaction does not progress. Under these conditions, the cell voltage of the galvanic cell remains constant indefinitely. The EMF is measured experimentally either using a potentiometer or by means of a high impedance voltmeter, which causes the current flowing through the galvanic cell to be negligible. Importantly, EMF measurements allow for the determination of relevant thermodynamic magnitudes (such as equilibrium constants, entropy variations, etc.).

As mentioned above, the EMF of an electrochemical cell is the voltage difference between its two electrodes. Accordingly, and if a "reduction criterion" is assumed, the EMF (E) of a galvanic cell can be calculated as:

$$E = E_+ - E_- \tag{1}$$

where E_+ and E_- are the reduction potential for the cathode and anode, respectively.

The potential of an individual electrode is given by equation (2):

$$E_{Ox/Red} = E^{o}_{Ox/Red} - \frac{RT}{nF} \ln \frac{\prod [Red]^{\alpha}}{\prod [Ox]^{\beta}} \tag{2}$$

Therefore, in the case of our example, the half-reaction occurring at each electrode and its corresponding potential is:

$$c\,\mathrm{C} + n\,\mathrm{e}^- \rightarrow d\,\mathrm{D} \qquad E_{\mathrm{C/D}} = E^{o}_{\mathrm{C/D}} - \frac{RT}{nF} \ln \frac{[\mathrm{D}]^d}{[\mathrm{C}]^c} \tag{3}$$

$$b\,\mathrm{B} + n\,\mathrm{e}^- \rightarrow a\,\mathrm{A} \qquad E_{\mathrm{B/A}} = E^{o}_{\mathrm{B/A}} - \frac{RT}{nF} \ln \frac{[\mathrm{A}]^a}{[\mathrm{B}]^b} \tag{4}$$

The combination of equation (3) and (4) yields the expression for the electromotive force of the galvanic cell:

$$E = E_+ - E_- = E^{o}_{\mathrm{C/D}} - \frac{RT}{nF} \ln \frac{[\mathrm{D}]^d}{[\mathrm{C}]^c} - \left(E^{o}_{\mathrm{B/A}} - \frac{RT}{nF} \ln \frac{[\mathrm{A}]^a}{[\mathrm{B}]^b} \right)$$

$$\mathrm{EMF} = E = E^{o}_{\mathrm{C/D}} - E^{o}_{\mathrm{B/A}} - \frac{RT}{nF} \ln \frac{[\mathrm{D}]^d\,[\mathrm{B}]^b}{[\mathrm{A}]^a\,[\mathrm{C}]^c} \tag{5}$$

Experimental procedure

1. Monitoring of a spontaneous redox reaction.

In a test tube, insert an iron nail into 2 mL of a copper(II) sulphate solution. Monitor the reaction over time and describe the changes observed at the iron nail surface during the reaction.

Write and balance the reaction that takes place in this experiment.

Useful data: E^{o} (Cu^{2+}/Cu) = 0.34 V; E^{o} (Fe^{2+}/Fe) = –0.44 V

2. Measurement of the EMF of galvanic cells.

For this part of the experiment, four different solutions will be used (they are already prepared in the laboratory):

- 50 mL of a 0.1 M $ZnSO_4$ solution.
- 50 mL of a 0.1 M $CuSO_4$ solution.
- 50 mL of a 0.2 M $K_3[Fe(CN)_6]$ solution.
- 50 mL of a 0.2 M $K_4[Fe(CN)_6]$ solution.

In two 100 mL beakers, put 50 mL of $ZnSO_4$ solution and 50 mL of $CuSO_4$ solution, respectively. In a third beaker, mix 25 mL of the potassium ferricyanide(III) solution and 25 mL of potassium ferrocyanide(II) solution.

Prepare the salt bridge by filling a U-shaped tube with a saturated KCl solution (already prepared in the laboratory) using a dropper, and afterwards by covering both ends of the tube with two cylinders made of filter paper and impregnated with KCl solution.

Clean the electrodes immediately before starting any measurement. The graphite electrode needs to be smoothly polished using filter paper. The zinc electrode is cleaned by immersing it for a few seconds (≤ 20 s) in diluted HCl (2:3 v/v). The copper electrode is cleaned by dipping the metallic piece for a few seconds (≤ 20 s) in diluted HNO_3 (2:3 v/v). Next, all the electrodes must be rinsed several times with deionized water.

Arrange the electrodes as shown in Figure 1:

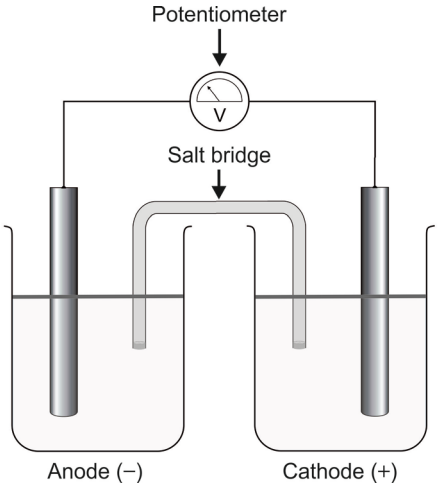


Figure 1. Schematic representation of an electrochemical cell and EMF measurement.

After immersing the electrodes in the corresponding solution, place the salt bridge in position and close the circuit by connecting the wires to the potentiometer. Check the setup with the teaching staff before measuring. Measuring the EMF requires you to wait for a stable value. Be careful to note the connection used in each experiment. Measure the EMF values three times and then calculate the average value from three valid trials.

Measure the EMF of galvanic cell 1: Zn | Zn^{2+} || $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$ | graphite

Measure the EMF of galvanic cell 2: Cu | Cu^{2+} || $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$ | graphite

Useful data:

E^o (Zn^{2+}/Zn) = –0.76 V; E^o (Cu^{2+}/Cu) = 0.34 V; E^o ($[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$) = 0.46 V.

3. Identification of the processes occurring in a singular galvanic cell.

Place a plastic Petri dish (ask the teaching staff for one) on white filter paper and add enough saturated KCl solution to fill the base of the Petri dish. Note that the lid of the Petri dish has two holes in it for you to pass the electrodes through.

Clean an iron cylinder with sandpaper and a graphite rod with filter paper and fit them into the holes in the lid of the Petri dish.

Without moving the plate, carefully add a drop of phenolphthalein around the graphite rod and a drop of potassium ferricyanide ($K_3[Fe(CN)_6]$) around the iron cylinder. Cover the plate.

Using a conductive wire, close the circuit connecting the alligator clips to the iron cylinder and the graphite rod. Monitor and write down the colour changes that occur over time.

Useful data: E^o (Fe^{2+}/Fe) = –0.44 V, E^o (O_2/OH^-) = 0.40 V

Safety and waste disposal

Dispose of the waste in the designated areas in the lab, as indicated in "*Pla de Gestió de Residus de la Docència Pràctica*" (see page 23).

Questions

Concerning Section 2

1. Explain why the electrodes should be pre-cleaned.
2. State the oxidation and reduction reactions that take place in galvanic cell 1.
3. State the oxidation and reduction reactions that take place in galvanic cell 2.
4. Write the expression for the cell potential of galvanic cell 1 as a function of the concentrations of the species involved.
5. Establish the comparison between the experimental results from galvanic cell 1 and those obtained by means of Nernst equation.
6. Write the expression for the cell potential of galvanic cell 2 as a function of the concentrations of the species involved.
7. Establish the comparison between the experimental results from galvanic cell 2 and those obtained by means of Nernst equation.

8. Justify why the measured cell voltage of galvanic cell 1 is greater than that of cell 2.
9. Explain what would happen if the two ends of the metals were connected directly.
10. Explain what happens when the electrodes are connected to the potentiometer. Does the oxidation–reduction reaction progress?
11. Propose another possible galvanic cell using the electrodes available.

Concerning Section 3

1. Explain which species are formed around the iron and graphite electrodes, respectively. Justify the colour changes observed around the electrodes placed in the Petri dish, taking into account that ferricyanide(III) reacts with iron(II) forming a complex known as Prussian blue.
2. Write out the reactions that take place at each electrode, and identify them as oxidation or reduction processes.
3. Justify whether this arrangement constitutes a galvanic cell. Establish the overall reaction and show the corresponding cell notation.
4. Write the expression for the cell potential as a function of the concentrations of the species involved.

EXPERIMENT 12 - POTENTIOMETRIC DETERMINATION OF THE TOTAL ACIDITY OF VINEGAR. ESTIMATION OF THE pK_a OF ACETIC ACID

Specific objectives

Preparation of solutions. Use of volumetric equipment.

Use of chemical and physical indicators. Calibration and use of a potentiometer (pH-meter). Measurement of the pH of a solution.

Potentiometric titration.

Determination of the concentration of acetic acid in a commercial sample. Estimation of the pK_a of acetic acid.

Independent work to be done before starting the experiment

Read Section J (*Ácidos y bases*) in the chapter *Fundamentos* (pages F72-F76) of the textbook *Principios de Química. Los caminos del descubrimiento*.

Read Section L3 (*Análisis volumétrico*) in the chapter *Fundamentos* (pages F89-F93) of the textbook *Principios de Química. Los caminos del descubrimiento*.

Read Sections 12.5 and 12.6 in Chapter 12 (pages 486-494) of the textbook *Principios de Química. Los caminos del descubrimiento*.

Draw a diagram of the experimental procedure and discuss it with the teaching staff.

Introduction

The pH of a solution depends on the acid strength (pK_a) of the different substances present and their concentration.

pH measurement is based on the difference in potential between a glass electrode and a reference electrode. A pH-meter transforms this difference of potential into a measure of the pH scale, and therefore H_3O^+ activity (or concentration in case of diluted aqueous solutions).

A potentiometric titration allows the quantitative monitoring of pH during acid–base titration. At the equivalence point, when the amount of OH^- (or H_3O^+) added as titrant is equal to the amount of acidic (or basic) analyte initially present in the solution, there is a sudden change in pH. The concentration of analyte can be determined from the inflection point of this sharp pH change, and the volume spent at the midpoint of the titration curve (half-neutralization) is a rough estimation of the pK_a value of the titrated compound.

According to the Spanish legislation (*Real Decreto* 661/2012, of 13th April), vinegar is the liquid suitable for human consumption resulting from the double alcoholic and acetic fermentation of agricultural products. For instance, wine vinegar is the product obtained exclusively by acetic fermentation of wine, which in turn is produced by alcoholic fermentation of sugars present in grape juice. The legal minimum acidity of vinegar, expressed in grams of acetic acid per 100 millilitres, is generally 5.0%, but 6.0% for wine vinegar. In addition to acetic acid, vinegar may contain different fixed and volatile acids (tartaric, lactic, citric, etc.) and other compounds (sugars, sulphates, chlorides, sulphur dioxide, artificial dyes, etc.).

Experimental procedure

1. Measuring the pH of different solutions.

Calibrate the pH-meter with the electrodes and the standard buffer solutions (ask the teaching staff). In beakers, not larger than 100 mL, prepare the following solutions (use a measuring cylinder) and measure their pH values. For a proper measurement using a combined glass pH electrode, both the membrane of the glass electrode and the external liquid junction of the reference electrode must be submerged in the sample solution. Rinse the combined electrode with deionized water before and after every use.

a) 10 mL 0.1 M hydrochloric acid + 40 mL deionized water

b) 10 mL 0.1 M acetic acid + 40 mL deionized water

c) 10 mL 0.1 M sodium chloride + 40 mL deionized water

d) 10 mL 0.1 M sodium acetate + 40 mL deionized water

e) 10 mL 0.1 M ammonia + 40 mL deionized water

f) 10 mL 0.1 M sodium hydroxide + 40 mL deionized water

g) 20 mL 0.1 M acetic acid + 20 mL 0.1 M sodium acetate + 10 mL deionized water

h) 20 mL 0.1 M acetic acid + 20 mL 0.1 M sodium acetate + 10 mL 0.1 M hydrochloric acid

i) 20 mL 0.1 M acetic acid + 20 mL 0.1 M sodium acetate + 10 mL 0.1 M sodium hydroxide

j) 20 mL 0.1 M acetic acid + 20 mL 0.1 M sodium acetate + 20 mL 0.1 M hydrochloric acid

k) 20 mL 0.1 M acetic acid + 20 mL 0.1 M sodium acetate + 20 mL 0.1 M sodium hydroxide

Calculate the final concentration of each protolyte in the mixtures and the expected pH value. Identify the mixtures leading to buffer solutions, and compare the measured and the calculated pH values.

2. Determination of the total acidity of vinegar.

Take the bottle containing the vinegar and check its degree of transparency. If any turbidity is observed, filter the sample using a glass funnel with filter paper. Pipette 10.00 mL of vinegar into a 100.00 mL volumetric flask and make the volume up to the mark with deionized water. Cap the flask and mix the solution thoroughly by inverting the flask and shaking it. Phenolphthalein or a pH-meter can be used as an indicator of the titration equivalence point.

2.1. Titration with a chemical indicator (phenolphthalein).

Pipette 10.00 mL of the diluted solution of vinegar into a 250 mL Erlenmeyer flask. Add about 50 mL of water, and three or four drops of phenolphthalein solution. Fill a 25.00 mL burette with a standardized 0.1 M solution of sodium hydroxide (ask the teaching staff). To properly clean the burette, first rinse it with deionized water and then with the titrant. Allow the solution to drain from the bottom by opening the stopcock. Fill the burette with titrant and completely open the stopcock to eliminate any bubbles at the tip. Finally, make up to the volume and the burette is ready for titration. Titrate the diluted solution of vinegar until a very slight pink colour remains for more than

thirty seconds. Note down the final burette reading as the end-point volume of the titration.

2.2. Titration with a physical indicator (pH-meter).

Potentiometric titrations can be carried out using a chemical indicator (phenolphthalein) at the same time.

Calibrate the pH-meter with the combined glass electrode and the standard buffer solutions. Prepare a table in your laboratory notebook to record the measured pH of the solution after each volume of titrant added.

Pipette 10.00 mL of the diluted solution of vinegar into a 100 mL beaker. Place the combined pH electrode, previously rinsed with water, in the beaker and add about 40 mL of deionized water to ensure the electrode bulb is completely submerged in the solution. Fill a 25.00 mL burette with the standardized solution of sodium hydroxide 0.1 mol L^{-1} and make up to the volume. Add measured volumes of titrant into the beaker, shake carefully after each addition, and record the pH-meter reading when stabilized.

At the beginning of the titration, add 1.00 mL volumes of sodium hydroxide solution from the burette. When approaching the equivalence point, it is necessary to make smaller additions of the titrant: finally about 0.05 mL, in the vicinity of the stoichiometric point. Provided that the same amount of sample is considered, the equivalence volume of titrant should be independent of the indicator employed (phenolphthalein or pH-meter). Thus, the millilitres of sodium hydroxide consumed in Section 2.1 should be the same amount needed to reach the equivalence point in Section 2.2. If the pK_a of the compound determined has to be estimated (see Subsection 3 of this experiment), small additions (0.10 mL) of the titrant in the vicinity of the half-neutralization point are convenient. Continue the addition of sodium hydroxide after the equivalence point until pH variations are small. Using a spreadsheet (e.g., Microsoft Excel), plot the pH of each point against the volume of titrant added, and find the equivalence volume (inflection point of the sharp pH change) by calculating and plotting the first derivative of the titration curve (examples of graphs can be found on pages 73 and 74).

Calculate the total acidity of the sample, expressed in grams of acetic acid per 100 mL of vinegar.

3. Estimation of the pK_a of acetic acid.

From the data collected in Subsection 2.2 and the equivalence volume established, determine the half-neutralization volume and the corresponding pH value. Estimate the acidity constant of the titrated compound.

Safety and waste disposal

When using pipettes, always use an appropriate liquid suction device, such as a pi-pump or aspirator pears. Never use your mouth!

Carefully insert the pipette into the suction device. Always hold it at the highest part so that it will not break when you insert it into the suction device.

Chemical compounds, especially if they are concentrated, can be dangerous. Always check the properties of those you use and take the appropriate precautions.

Dispose of the waste in the designated areas in the lab, as indicated in "*Pla de Gestió de Residus de la Docència Pràctica*" (see pages 23 and 24).

Questions

1. What error would you make when titrating if there were air bubbles in the tip of the burette?
2. Is any type of error committed when we dilute the vinegar solution with water inside the Erlenmeyer flask, before proceeding with its titration?
3. According to the titration curve obtained in Subsection 2.2, propose chemical indicators alternative to phenolphthalein.
4. Justify the pH of the equivalence point of the acetic acid titration with sodium hydroxide. If the analyte were a strong acid, such as hydrochloric acid, what would the pH be?

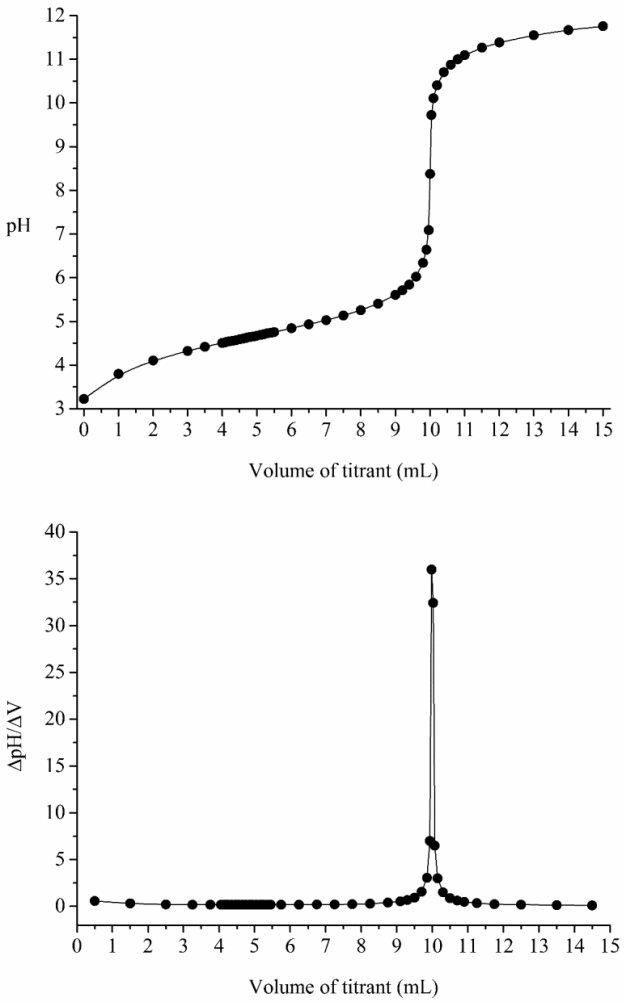
A. Example of a titration curve and plot of its first derivative (Subsection 2.2.):

These tables and plots are for illustrative purposes only; the equivalence volume depends on the acidity of the particular vinegar sample and the titrant concentration.

Obs.	*Titration curve*		*First derivative*	
	V_{NaOH} (mL)	pH	V_{NaOH} (mL)[(a)]	$\Delta pH/\Delta V$[(b)]
1	0.00	3.22	0.50	0.57
2	1.00	3.80	1.50	0.31
3	2.00	4.11	2.50	0.22
4	3.00	4.32	3.25	0.19
5	3.50	4.42	3.75	0.18
6	4.00	4.51	4.05	0.17
7	4.10	4.52	4.15	0.17
8	4.20	4.54	4.25	0.17
9	4.30	4.56	4.35	0.17
10	4.40	4.57	4.45	0.17
11	4.50	4.59	4.55	0.17
12	4.60	4.61	4.65	0.17
13	4.70	4.62	4.75	0.17
14	4.80	4.64	4.85	0.17
15	4.90	4.66	4.95	0.17
16	5.00	4.67	5.05	0.17
17	5.10	4.69	5.15	0.17
18	5.20	4.71	5.25	0.17
19	5.30	4.72	5.35	0.17
20	5.40	4.74	5.45	0.17
21	5.50	4.76	5.75	0.17
22	6.00	4.84	6.25	0.18
23	6.50	4.93	6.75	0.19
24	7.00	5.03	7.25	0.21
25	7.50	5.13	7.75	0.24
26	8.00	5.26	8.25	0.30
27	8.50	5.41	8.75	0.40
28	9.00	5.60	9.10	0.53
29	9.20	5.71	9.30	0.67
30	9.40	5.84	9.50	0.92
31	9.60	6.03	9.70	1.55
32	9.80	6.34	9.85	3.05
33	9.90	6.64	9.93	6.98
34	9.96	7.09	**9.98**	**35.98**
35	10.00	8.38	10.02	32.42
36	10.04	9.73	10.07	6.49
37	10.10	10.11	10.15	3.00
38	10.20	10.41	10.30	1.49
39	10.40	10.71	10.50	0.87
40	10.60	10.88	10.70	0.61
41	10.80	11.00	10.90	0.47
42	11.00	11.10	11.25	0.34
43	11.50	11.27	11.75	0.24
44	12.00	11.39	12.50	0.17
45	13.00	11.55	13.50	0.12
46	14.00	11.67	14.50	0.09
47	15.00	11.76	-	-

[(a)] $(V_{n+1} + V_n) / 2$

[(b)] $(pH_{n+1} - pH_n) / (V_{n+1} - V_n)$



B. Example of the pK_a estimation of acetic acid from the titration curve (Section 3):

$$K_a \approx \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} \approx \frac{\left(10^{-pH}\right)^* \left(\frac{\text{moles of } CH_3COO^-}{\cancel{\text{volume of solution}}}\right)^*}{\left(\frac{\text{moles of } CH_3COOH^-}{\cancel{\text{volume of solution}}}\right)^*} = \frac{\left(10^{-pH}\right)^* \left(\text{moles of } CH_3COO^-\right)^*}{\left(\text{moles of } CH_3COOH\right)^*}$$

$$\left(\text{moles of } CH_3COO^-\right)^* \approx V_{NaOH}\,\cancel{(mL)} \times \frac{C_{NaOH}\ \cancel{\text{moles of NaOH}}}{10^3\ \cancel{mL}} \times \frac{1\ \cancel{\text{mole of } CH_3COOH}}{1\ \cancel{\text{mole of NaOH}}} \times \frac{1 \text{ mole of } CH_3COO^-}{1\ \cancel{\text{mole of } CH_3COOH}}$$

$$\left(\text{moles of } CH_3COOH\right)^* = \left(\text{initial moles of } CH_3COOH\right)^{\#} - \left(\text{moles of } CH_3COO^-\right)^*$$

$$\left(\text{initial moles of } CH_3COOH\right)^{\#} \approx V_{NaOH,\text{end-point}}\,\cancel{(mL)} \times \frac{C_{NaOH}\ \cancel{\text{moles of NaOH}}}{10^3\ \cancel{mL}} \times \frac{1 \text{ mole of } CH_3COOH}{1\ \cancel{\text{mole of NaOH}}}$$

*at a particular point in the titration after addition of V_{NaOH} mL

$^{\#}$before starting the titration

(since acetic is a weak acid, it is assumed that the amount of CH_3COO^- is negligible in relation to CH_3COOH)

$V_{NaOH,end\text{-}point}$ (mL)	C_{NaOH} (M)
9.98	0.100

Obs.	V_{NaOH} (mL)	pH	$[H_3O^+]$ (M)	moles of CH_3COO^-	moles of CH_3COOH	K_a	pK_a	
6	4.00	4.51	3.12E-05	4.00E-04	5.98E-04	2.09E-05	4.68	
7	4.10	4.52	3.00E-05	4.10E-04	5.88E-04	2.09E-05	4.68	
8	4.20	4.54	2.89E-05	4.20E-04	5.78E-04	2.10E-05	4.68	
9	4.30	4.56	2.78E-05	4.30E-04	5.68E-04	2.10E-05	4.68	
10	4.40	4.57	2.67E-05	4.40E-04	5.58E-04	2.11E-05	4.68	
11	4.50	4.59	2.57E-05	4.50E-04	5.48E-04	2.11E-05	4.68	
12	4.60	4.61	2.47E-05	4.60E-04	5.38E-04	2.12E-05	4.67	
13	4.70	4.62	2.38E-05	4.70E-04	5.28E-04	2.12E-05	4.67	
14	4.80	4.64	2.29E-05	4.80E-04	5.18E-04	2.12E-05	4.67	
15	4.90	4.66	2.21E-05	4.90E-04	5.08E-04	2.13E-05	4.67	
16	**5.00**	**4.67**	**2.12E-05**	**5.00E-04**	**4.98E-04**	**2.13E-05**	**4.67**	(a)
17	5.10	4.69	2.04E-05	5.10E-04	4.88E-04	2.14E-05	4.67	
18	5.20	4.71	1.97E-05	5.20E-04	4.78E-04	2.14E-05	4.67	
19	5.30	4.72	1.89E-05	5.30E-04	4.68E-04	2.14E-05	4.67	
20	5.40	4.74	1.82E-05	5.40E-04	4.58E-04	2.15E-05	4.67	
21	5.50	4.76	1.75E-05	5.50E-04	4.48E-04	2.15E-05	4.67	
22	6.00	4.84	1.44E-05	6.00E-04	3.98E-04	2.17E-05	4.66	
						Mean	**4.67**	

(a) ≈ Half-neutralization point ([CH_3COOH] = [CH_3COO^-]).

EXPERIMENT 13 - KINETICS OF THE REACTION OF A FOOD DYE WITH BLEACH

Specific objectives

Use of a spectrophotometer to record absorption spectra.

Determination of individual reaction orders (partial reaction orders) for each reactant.

Determination of the rate constant of a chemical reaction.

Independent work to be done before starting the experiment

Read Sections 14.1-14.6 in Chapter 14 (pages 561-580) of the textbook *Principios de Química. Los caminos del descubrimiento*.

Review the integrated rate laws for zero-, first- and second-order reactions.

Draw a diagram of the experimental procedure and discuss it with the teaching staff.

Introduction

Erythrosine and Brilliant Blue (Figure 1) are intensely coloured organic substances (red and blue, respectively), which are widely used in the food industry. When coloured solutions of these dyes are treated with bleach, an aqueous solution of sodium hypochlorite (NaClO), their colour gradually disappears until they become completely colourless. In this experiment, the reaction of either Erythrosine or Brilliant Blue with hypochlorite ions will be monitored spectrophotometrically.

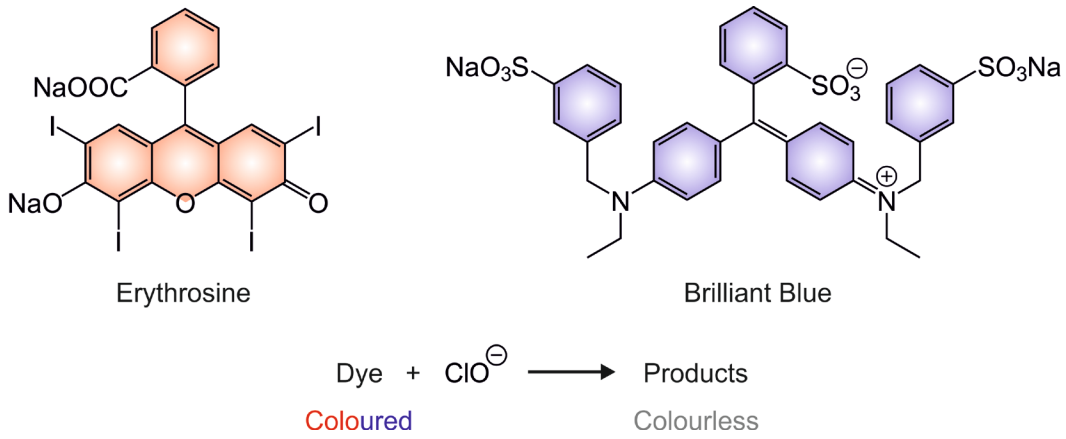


Figure 1. Chemical structures of Erythrosine and Brilliant Blue and chemical reaction of the dyes with bleach.

The rate of a chemical reaction is determined by its rate law. For a reaction with two reactants such as A + B → C, the rate law (or rate equation) can be expressed as:

$$v = k\,[A]^{\alpha}\,[B]^{\beta} \qquad (1)$$

where k is the rate constant for the reaction and α and β are the individual reaction orders (partial reaction orders) for each reactant. While the rate constant depends on the experimental conditions under which the reaction is carried out (temperature, solvent, etc.), the individual

reaction orders are given by the mechanism through which the reaction proceeds. When the chemical reaction involves ionic species, the ionic strength also affects the rate constant (primary kinetic salt effect). However, if a large excess of one of the ionic reactants is used, the ionic strength of the reaction medium is virtually constant and, therefore, it is not necessary to consider this effect.

The rate law for the reaction between either Erythrosine or Brilliant Blue and bleach can be expressed, at a constant temperature *T*, as:

$$v = k\,[\mathrm{ClO^-}]^{\alpha}\,[\mathrm{dye}]^{\beta} \tag{2}$$

In this experiment, a significant excess of hypochlorite ions will be present in the reaction medium. As a consequence, $[\mathrm{ClO^-}]$ will be essentially constant during the reaction. Therefore, the rate law for the reaction can be rewritten as:

$$v = k'\,[\mathrm{dye}]^{\beta} \tag{3}$$

where k' is the apparent rate constant of the reaction and $k' = k \cdot [\mathrm{ClO^-}]^{\alpha}$.

The partial reaction order with respect to the dye, β, can be determined by means of an integral method, that is, by fitting the experimental data to the corresponding integrated rate equations. For this purpose, the concentration of the dye (zero-order), the natural logarithm of the concentration of the dye (first-order) and the inverse of the concentration of the dye (second-order) are plotted against time. The plot that best fits the experimental data, i.e., the one that yields the optimum linear regression, indicates the partial reaction order with respect to the dye.

The partial reaction order with respect to $\mathrm{ClO^-}$ can be determined by comparing the slopes of the graphs when the dye concentration is constant but the initial bleach concentration is modified. If two different trials (1 and 2) are performed under these experimental conditions, the corresponding apparent rate constants (k_1' and k_2') can be expressed as follows:

$$k_1' = k\,[\mathrm{ClO^-}]_1^{\alpha} \qquad \text{and} \qquad k_2' = k\,[\mathrm{ClO^-}]_2^{\alpha} \tag{4}$$

Consequently, the partial reaction order with respect to $\mathrm{ClO^-}$, α, can be calculated as:

$$\alpha = \frac{\ln\left(\frac{k_1'}{k_2'}\right)}{\ln\left(\frac{[\mathrm{ClO^-}]_1}{[\mathrm{ClO^-}]_2}\right)} \tag{5}$$

The rate law and the rate constant of a reaction can be determined experimentally by following the evolution of the concentration of a specific reactant or product over time. The spectrophotometric method is one of the most conventional strategies used for this purpose. In this method, the absorbance of the reaction mixture is constantly monitored as the reaction proceeds. The measured absorbance (*A*) can be related to the concentration of the absorbing species (*c* in mol $\mathrm{L^{-1}}$) by means of the well-known Lambert-Beer law:

$$A = \varepsilon_{\lambda} \cdot l \cdot c \tag{6}$$

where l is the optical path length (i.e., the distance that the light travels through the solution, see Figure 1 in Experiment 8) and ε_λ is the molar absorption coefficient (in mol^{-1} L cm^{-1}) at a specific wavelength, λ.

In this particular reaction, the only coloured substance, that is, the only substance that absorbs light in the visible region of the electromagnetic spectrum, is the dye (Erythrosine or Brilliant Blue). Meanwhile, the hypochlorite ion and the products formed are colourless, i.e., they do not absorb light within this range of wavelengths. Therefore, in this case, spectrophotometric monitoring of the reaction tracks the evolution of the concentration of the dye.

Absorbance will be measured with a spectrophotometer at the wavelength of maximum absorption (λ_{Max}), i.e., the wavelength at which the dye absorbs the most. In order to determine λ_{Max}, an absorption spectrum will be recorded for each dye from 400 nm to 800 nm (visible spectrum).

Experimental procedure

Ask the teaching staff to assign you one of the two dyes.

1. Preparation of the reactant solutions.

Option A: Kinetic study of the reaction of Erythrosine with bleach.

Three solutions will be needed: solution **A**, solution **B** and a NaClO solution.

Prepare solution **A** from the 6.8×10^{-4} M stock solution of Erythrosine available in the laboratory. Take an aliquot of 20.00 mL of the stock solution with a pipette and add it to a 100.00 mL volumetric flask, dilute it with deionized water and set the meniscus to the volume mark. Calculate the concentration of Erythrosine in solution **A**.

Take an aliquot of 10.00 mL of solution **A** with a pipette and add it to a 100.00 mL volumetric flask, dilute it with deionized water and set the meniscus to the volume mark. Calculate the concentration of Erythrosine in solution **B**.

Prepare 100 mL of a 0.5 M NaClO solution from fresh household bleach. Household bleach is a 1 M NaClO solution. Take the calculated volume with a pipette and add it to a 100.00 mL volumetric flask, dilute it with deionized water and set the meniscus to the volume mark.

Option B: Kinetic study of the reaction of Brilliant Blue with bleach.

Four solutions will be needed: solution **A**, solution **B** and two NaClO solutions.

Prepare solution **A** from the 1.0×10^{-4} M stock solution of Brilliant Blue available in the laboratory. Take an aliquot of 25.00 mL of the stock solution with a pipette and add it to a 100.00 mL volumetric flask, dilute it with deionized water and set the meniscus to the volume mark. Calculate the concentration of Brilliant Blue in solution **A**.

Take an aliquot of 20.00 mL of solution **A** with a pipette and add it to a 100.00 mL volumetric flask, dilute it with deionized water and set the meniscus to the volume mark. Calculate the concentration of Erythrosine in solution **B**.

Prepare 100 mL of a 0.1 M NaClO solution and 100 mL of a 0.2 M NaClO solution from fresh household bleach. Household bleach is a 1 M NaClO solution. Take the calculated

volumes with a pipette and add them to 100.00 mL volumetric flasks, dilute them with deionized water and set the meniscuses to the volume marks.

2. Determination of the wavelength of maximum absorption (λ_{Max}) of the dye.

Record, using solution **B**, the absorption spectrum of the assigned dye with the spectrophotometer. Read the standard operating protocol (SOP) available in the laboratory before using the instrument. Determine the wavelength of maximum absorption (λ_{Max}) from the absorption spectrum and complete the following table:

Dye	ε ($10^4 \cdot M^{-1} \cdot cm^{-1}$)	λ_{Max} (nm)
Erythrosine	8	…
Brilliant Blue	11	…

3. Spectrophotometric monitoring of the reaction of the dye with bleach.

Take four clean and dry beakers and prepare the following contents (only those corresponding to the assigned dye).

Dye	Beaker 1	Beaker 2	Beaker 3	Beaker 4
Erythrosine	10 mL *Solution B*	10 mL *Solution B*	10 mL NaClO 1 M	10 mL NaClO 0.5 M
Brilliant Blue	10 mL *Solution B*	10 mL *Solution B*	10 mL NaClO 0.2 M	10 mL NaClO 0.1 M

For each dye, two trials will be carried out:

1) Trial 1: s*olution B* of the assigned dye with diluted NaClO (0.5 M for Erythrosine and 0.1 M for Brilliant Blue), i.e., beakers 1 + 3.

2) Trial 2: *solution B* of the assigned dye with a more concentrated solution of NaClO (1 M for Erythrosine and 0.2 M for Brilliant Blue).

Determine the concentration of the dye and hypochlorite ion that will be present in the reaction medium in each trial. Complete the following table (only the part corresponding to the assigned dye!) before starting the kinetic monitoring of the reaction.

Dye	Trial	Beakers	Added dye	Added NaClO	[dye] (M)	[ClO^-] (M)
Erythrosine	**1**	1 + 3	10 mL *Solution B*	10 mL NaClO 1 M	…	…
	2	2 + 4	10 mL *Solution B*	10 mL NaClO 0.5 M	…	…
Brilliant Blue	**1**	1 + 3	10 mL *Solution B*	10 mL NaClO 0.2 M	…	…
	2	2 + 4	10 mL *Solution B*	10 mL NaClO 0.1 M	…	…

To monitor the reaction spectrophotometrically, select the *kinetics mode* on the instrument and set the following parameters: run time = 600 s, read interval = 15 s and lag time = 0 s.

Remember that all kinetic studies should be performed at the wavelength of maximum absorption of the assigned dye (see Section 2 above).

Pour the ClO^- solution into the beaker that contains the solution of the dye. Mix and homogenize the content quickly and transfer a small volume to the cuvette. The reaction time starts (t = 0) when the ClO^- solution is added to the dye. Use a chronometer to measure how long it takes you and your partner to mix both solutions and start the data collection (this time should be considered later in the data processing). Collect data until the absorbance of the solution is less than 0.1.

4. Data processing and analysis.

The data collected are in a document in the USB: they will consist of a table of absorbance as a function of time. Copy the results to a Microsoft Excel spreadsheet.

Calculate the concentration at each reaction time using the Lambert-Beer law.

Add to the initial time the time you spent mixing the solutions and placing the cuvette in the instrument.

Obtain a table of concentration against time.

Establish the partial reaction order with respect to the dye using the integrated rate laws, i.e., plot c versus time, ln(c) versus time and 1/c versus time.

Determine the apparent rate constant and the rate constant.

Calculate the partial reaction order with respect to ClO^-.

Determine graphically the initial concentration of the dye and compare it with the actual value.

Safety and waste disposal

Dispose of the waste in the designated areas in the lab, as indicated in "*Pla de Gestió de Residus de la Docència Pràctica*" (see page 24).

Questions

1. Consider the generic reaction A + B → C and assume that the reaction product is brightly coloured.
   a) What will happen to the absorbance of C, monitored at its wavelength of maximum absorption, as the reaction progresses?
   b) Suppose you carry out the reaction mentioned above using a large excess of B. If the reaction is first-order in A, would the graph of ln [A] versus time be linear?
2. Could we carry out the same experiment performed here (the reaction of Erythrosine or Brilliant Blue with bleach) but using a large excess of the dye?

ANNEXES

GHS Hazard Pictograms:

		
GHS01 Danger Unstable, Explosive	GHS02 Danger or Warning Flammable	GHS03 Danger or Warning Oxidising
		
GHS04 Warning Compressed gas	GHS05 Danger or Warning Corrosive cat. 1	GHS06 Danger Toxic cat. 1-3
		
GHS07 Warning Toxic cat. 4 Irritant cat. 2 or 3 Lower systemic health hazards	GHS08 Danger or Warning Systemic health hazards	GHS09 Warning (for cat. 1) Environment

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22 April 2019

The EU-GHS Hazard statements in English
(Precautionary statements: see page 5)

Updated according to the 12th ATP of the CLP regulation of March 28, 2019
(12th ATP = regulation (EU) 2019/521)
The modifications introduced by the 12th ATP are highlighted.

H Codes	H Phrases
H200	Unstable explosives.
H201	Explosive; mass explosion hazard.
H202	Explosive, severe projection hazard.
H203	Explosive; fire, blast or projection hazard.
H204	Fire or projection hazard.
H205	May mass explode in fire.
H206	Fire, blast or projection hazard; increased risk of explosion if desensitising agent is reduced.
H207	Fire or projection hazard; increased risk of explosion if desensitising agent is reduced.
H208	Fire hazard; increased risk of explosion if desensitising agent is reduced.
H220	Extremely flammable gas.
H221	Flammable gas.
H222	Extremely flammable aerosol.
H223	Flammable aerosol.
H224	Extremely flammable liquid and vapour.
H225	Highly flammable liquid and vapour.
H226	Flammable liquid and vapour.
H228	Flammable solid.
H229	Pressurised container: May burst if heated.
H230	May react explosively even in the absence of air.
H231	May react explosively even in the absence of air at elevated pressure and/or temperature.
H232	May ignite spontaneously if exposed to air.
H240	Heating may cause an explosion.
H241	Heating may cause a fire or explosion.
H242	Heating may cause a fire.
H250	Catches fire spontaneously if exposed to air.
H251	Self-heating: may catch fire.
H252	Self-heating in large quantities; may catch fire.
H260	In contact with water releases flammable gases which may ignite spontaneously.
H261	In contact with water releases flammable gases.
H270	May cause or intensify fire; oxidizer.
H271	May cause fire or explosion; strong oxidizer.

H Codes	H Phrases
H272	May intensify fire; oxidizer.
H280	Contains gas under pressure; may explode if heated.
H281	Contains refrigerated gas; may cause cryogenic burns or injury.
H290	May be corrosive to metals.
H300	Fatal if swallowed.
H301	Toxic if swallowed.
H302	Harmful if swallowed.
H304	May be fatal if swallowed and enters airways.
H310	Fatal in contact with skin.
H311	Toxic in contact with skin.
H312	Harmful in contact with skin.
H314	Causes severe skin burns and eye damage.
H315	Causes skin irritation.
H317	May cause an allergic skin reaction.
H318	Causes serious eye damage. (not needed beside H314)
H319	Causes serious eye irritation.
H330	Fatal if inhaled.
H331	Toxic if inhaled.
H332	Harmful if inhaled.
H334	May cause allergy or asthma symptoms or breathing difficulties if inhaled.
H335	May cause respiratory irritation.
H336	May cause drowsiness or dizziness.
H340	May cause genetic defects <*state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard*>.
H341	Suspected of causing genetic defects <*state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard*>.
H350	May cause cancer <*state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard*>.
H351	Suspected of causing cancer <*state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard*>.
H360	May damage fertility or the unborn child <*state specific effect if known* > <*state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard*>.
H361	Suspected of damaging fertility or the unborn child <*state specific effect if known*> <*state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard*>.
H362	May cause harm to breast-fed children.
H370	Causes damage to organs <*or state all organs affected, if known*> <*state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard*>.
H371	May cause damage to organs <*or state all organs affected, if known*> <*state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard*>.
H372	Causes damage to organs <*or state all organs affected, if known*> through prolonged or repeated exposure <*state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard*>.

H Codes	H Phrases
H373	May cause damage to organs *<or state all organs affected, if known>* through prolonged or repeated exposure *<state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>*.
H300 + H310	Fatal if swallowed or in contact with skin.
H300 + H330	Fatal if swallowed or if inhaled.
H310 + H330	Fatal in contact with skin or if inhaled.
H300 + H310 + H330	Fatal if swallowed, in contact with skin or if inhaled.
H301 + H311	Toxic if swallowed or in contact with skin.
H301 + H331	Toxic if swallowed or if inhaled.
H311 + H331	Toxic in contact with skin or if inhaled.
H301 + H311 + H331	Toxic if swallowed, in contact with skin or if inhaled.
H302 + H312	Harmful if swallowed or in contact with skin.
H302 + H332	Harmful if swallowed or if inhaled.
H312 + H332	Harmful in contact with skin or if inhaled.
H302 + H312 + H332	Harmful if swallowed, in contact with skin or if inhaled.
H400	Very toxic to aquatic life.
H410	Very toxic to aquatic life with long lasting effects.
H411	Toxic to aquatic life with long lasting effects.
H412	Harmful to aquatic life with long lasting effects.
H413	May cause long lasting harmful effects to aquatic life.
H420	Harms public health and the environment by destroying ozone in the upper atmosphere.

EUH Codes

EUH Code	EUH Phrases
EUH014	Reacts violently with water.
EUH018	In use may form flammable/explosive vapour-air mixture.
EUH019	May form explosive peroxides.
EUH029	Contact with water liberates toxic gas.
EUH031	Contact with acids liberates toxic gas.
EUH032	Contact with acids liberates very toxic gas.
EUH044	Risk of explosion if heated under confinement.
EUH066	Repeated exposure may cause skin dryness or cracking.
EUH070	Toxic by eye contact
EUH071	Corrosive to the respiratory tract.
EUH201 EUH201A	Contains lead. Should not be used on surfaces liable to be chewed or sucked by children. Warning! Contains lead.
EUH202	Cyanoacrylate. Danger. Bonds skin and eyes in seconds. Keep out of the reach of children.
EUH203	Contains chromium (VI). May produce an allergic reaction.
EUH204	Contains isocyanates. May produce an allergic reaction.
EUH205	Contains epoxy constituents. May produce an allergic reaction.
EUH206	Warning! Do not use together with other products. May release dangerous gases (chlorine).

EUH207	Warning! Contains cadmium. Dangerous fumes are formed during use. See information supplied by the manufacturer. Comply with the safety instructions.
EUH208	Contains (name of sensitising substance). May produce an allergic reaction. (EUH08 may be omitted if EUH204 or EUH205 has to be applied.)
EUH209 EUH209A	Can become highly flammable in use. Can become flammable in use.
EUH210	Safety data sheet available on request
EUH401	To avoid risks to human health and the environment, comply with the instructions for use.

The EU-GHS precautionary statements in English

Update according to the 12th ATP of 28th March 2019 of the CLP regulation
(12th ATP = regulation (EU) 2019/521)
If only the P code is highlighted, this means that the text of the P phrase remains unchanged, but the criteria for its selection have been modified. This may also be the case if the text has been modified, even if the P code is not highlighted. If a P phrase is new, the whole text including the P-code is highlighted.
When a forward slash [/] appears in a P phrase, this indicates that a choice has to be made between the phrases they separate in accordance with the indications provided in annex IV of the CLP regulation.
The "Guidance on Labelling and Packaging in accordance with Regulation (EC) No 1272/2008"
(of July 2017) contains a guidance on the selection of the P phrases in chapter 7.

P Codes	P Phrases
P101	If medical advice is needed, have product container or label at hand.
P102	Keep out of reach of children.
P103	Read carefully and follow all instructions. (omit where P202 is used)
P201	Obtain special instructions before use.
P202	Do not handle until all safety precautions have been read and understood.
P210	Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P211	Do not spray on an open flame or other ignition source.
P212	Avoid heating under confinement or reduction of the desensitising agent.
P220	Keep away from clothing and other combustible materials.
P222	Do not allow contact with air.
P223	Do not allow contact with water.
P230	Keep wetted with…
P231	Handle and store contents under inert gas/…
P232	Protect from moisture.
P233	Keep container tightly closed.
P234	Keep only in original packaging.
P235	Keep cool.
P240	Ground and bond container and receiving equipment.
P241	Use explosion-proof [electrical/ventilating/lighting/…] equipment.
P242	Use non-sparking tools.
P243	Take action to prevent static discharges.
P244	Keep valves and fittings free from oil and grease.
P250	Do not subject to grinding/shock/friction/…
P251	Do not pierce or burn, aven after use.
P260	Do not breathe dust/fume/gas/mist/vapours/spray.
P261	Avoid breathing dust/fume/gas/mist/vapours/spray.
P262	Do not get in eyes, on skin, or on clothing.
P263	Avoid contact during pregnancy and while nursing.
P264	Wash … thoroughly after handling.
P270	Do no eat, drink or smoke when using this product.
P271	Use only outdoors or in a well-ventilated area.

P272	Contaminated work clothing should not be allowed out of the workplace.
P273	Avoid release to the environment.
P280	Wear protective gloves/protective clothing/eye protection/face protection/ hearing protection/…
P282	Wear cold insulating gloves and either face shield or eye protection.
P283	Wear fire resistant or flame-retardant clothing.
P284	[In case of inadequate ventilation] wear respiratory protection.
P231+P232	Handle and store contents under inert gas/… Protect from moisture.
P301	IF SWALLOWED:
P302	IF ON SKIN:
P303	IF ON SKIN (or hair):
P304	IF INHALED:
P305	IF IN EYES:
P306	IF ON CLOTHING:
P308	IF exposed or concerned:
P310	Immediately call a POISON CENTER/doctor/…
P311	Call a POISON CENTER/doctor/….
P312	Call a POISON CENTER/doctor/… if you feel unwell.
P313	Get medical advice/attention.
P314	Get medical advice/attention if you feel unwell.
P315	Get immediate medical advice/attention.
P320	Specific treatment is urgent (see … on this label).
P321	Specific treatment (see … on this label).
P330	Rinse mouth.
P331	Do NOT induce vomiting.
P332	If skin irritation occurs:
P333	If skin irritation or rash occurs:
P334	Immerse in cool water [or wrap in wet bandages].
P335	Brush off loose particles from skin.
P336	Thaw frosted parts with lukewarm water. Do no rub affected area.
P337	If eye irritation persists:
P338	Remove contact lenses, if present and easy to do. Continue rinsing.
P340	Remove person to fresh air and keep comfortable for breathing.
P342	If experiencing respiratory symptoms:
P351	Rinse cautiously with water for several minutes.
P352	Wash with plenty of water/…
P353	Rinse skin with water [or shower].
P360	Rinse immediately contaminated clothing and skin with plenty of water before removing clothes.
P361	Take off immediately all contaminated clothing.
P362	Take off contaminated clothing.
P363	Wash contaminated clothing before reuse.

P364	And wash it before reuse.
P370	In case of fire:
P371	In case of major fire and large quantities:
P372	Explosion risk.
P373	DO NOT fight fire when fire reaches explosives.
P375	Fight fire remotely due to the risk of explosion.
P376	Stop leak if safe to do so.
P377	Leaking gas fire: Do not extinguish, unless leak can be stopped safely.
P378	Use … to extinguish.
P380	Evacuate area.
P381	In case of leakage, eliminate all ignition sources.
P390	Absorb spillage to prevent material damage.
P391	Collect spillage.
P301+P310	IF SWALLOWED: Immediately call a POISON CENTER/doctor/….
P301+P312	IF SWALLOWED: Call a POISON CENTER/doctor/… if you feel unwell.
P301+P330+P331	IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.
P302+P334	IF ON SKIN: Immerse in cool water [or wrap in wet bandages].
P302+P335+P334	IF ON SKIN: Brush off loose particles from skin. Immerse in cool water [or wrap in wet bandages].
P302+P352	IF ON SKIN: Wash with plenty of water/…
P303+P361+P353	IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water [or shower].
P304+P340	IF INHALED: Remove person to fresh air and keep comfortable for breathing.
P305+P351+P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P306+P360	IF ON CLOTHING: rinse immediately contaminated clothing and skin with plenty of water before removing clothes.
P308+P311	IF exposed or concerned: Call a POISON CENTER/doctor/…
P308+P313	IF exposed or concerned: Get medical advice/attention.
P332+P313	If skin irritation occurs: Get medical advice/attention.
P333+P313	If skin irritation or rash occurs: Get medical advice/attention.
P336+P315	Thaw frosted parts with lukewarm water. Do not rub affected area. Get immediate medical advice/attention.
P337+P313	If eye irritation persists: Get medical advice/attention.
P342+P311	If experiencing respiratory symptoms: Call a POISON CENTER/doctor/…
P361+P364	Take off immediately all contaminated clothing and wash it before reuse.
P362+P364	Take off contaminated clothing and wash it before reuse.
P370+P376	In case of fire: Stop leak if safe to do so.
P370+P378	In case of fire: Use … to extinguish.
P370+P372+P380+ P373	In case of fire: Explosion risk. Evacuate area. DO NOT fight fire when fire reaches explosives.
P370+P380+P375	In case of fire: Evacuate area. Fight fire remotely due to the risk of explosion.
P370+P380+P375 [+P378]	In case of fire: Evacuate area. Fight fire remotely due to the risk of explosion. [Use … to extinguish].

P371+P380+P375	In case of major fire and large quantities: Evacuate area. Fight fire remotely due to the risk of explosion.
P401	Store in accordance with…
P402	Store in a dry place.
P403	Store in a well-ventilated place.
P404	Store in a closed container.
P405	Store locked up.
P406	Store in a corrosion resistant/… container with a resistant inner liner.
P407	Maintain air gap between stacks or pallets.
P410	Protect from sunlight.
P411	Store at temperatures not exceeding …°C/…°F.
P412	Do not expose to temperatures exceeding 50°C/ 122°F.
P413	Store bulk masses greater than … kg/… lbs at temperatures not exceeding …°C/…°F.
P420	Store separately.
P402+P404	Store in a dry place. Store in a closed container.
P403+P233	Store in a well-ventilated place. Keep container tightly closed.
P403+P235	Store in a well-ventilated place. Keep cool.
P410+P403	Protect from sunlight. Store in a well-ventilated place.
P410+P412	Protect from sunlight. Do not expose to temperatures exceeding 50°C/ 122°F.
P501	Dispose of contents/container to …
P502	Refer to manufacturer or supplier for information on recovery or recycling.
P503	Refer to manufacturer/ supplier/… for information on disposal/recovery/ recycling