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ANALYTICAL CHEMISTRY

Recommended
by the Ministry of Education and Science of Ukraine as the Manual for
the Students of Institutions of Higher Education

Kyiv

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Рекомендовано Міністерством освіти і науки України як навчальний посібник для студентів вищих навчальних закладів (лист №1/ІІ-688 від 10.02.2010 р.)
Рекомендовано Вченою радою природничо-гуманітарного ННІ Національного університету біоресурсів і природокористування України для студентів факультету екології і сталого розвитку спеціальності ,,Екологія і охорона навколишнього середовища,, , для яких викладання проводиться англійською мовою (протокол № 10 від 21.06.2012 р.)

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Analytical Chemistry: Навчальний посібник для студентів вищих навчальних закладів // Л.В.Войтенко, В.Є.Косматий, В.А.Копілевич, Р.В.Лаврик. – 214с.

Навчальний посібник складається з двох взаємопов'язаних частин, що відносяться до хімічного аналізу – якісного і кількісного. У якісному аналізі студентам пропонується вивчення найважливіших біогенних катіонів і аніонів, принципи і методики встановлення складу речовин. У кількісному аналізі розглянуто методи досліджень, які є теоретичною базою аналізу грунтів, агрохімікатів, рослинних метеріалів, продуктів харчування. Теоретичний матеріал курсу аналітичної хімії та додатки подано блочно до окремих розділів посібника.

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Analytical Chemistry: Manual for the Students of Institutions of Higher Education // L.V.Voytenko, V.E.Kosmatiy, V.A.Kopilevich, R.V.Lavryk. – 214p.

The manual consists of two parts covering chemical analysis – qualitative and quantative. Qualitative analysis studies the most important biogenic cations and anions, principles and methods of defining the contents of substances. Quantative analysis describes research methods which constitute theoretical basis of analysing soils, agrochemicals, plant materials, food staffs. Theoretical material of the course on analytical chemistry and appendixes are offered in units to different chapters of the manual.

ISBN

CONTENT

CHAPTER 1. INTRODUCTION

Vocabulary

English	**Українська назва**	**English**	**Українська назва**
Pesticide	Пестицид	Salicylic acid	Саліцилова кислота
Pharmaceutical	Фармацевтичний препарат	Catalyst	Каталіз
Alloy	Сплав	Ore	Руда
Quantitative analysis	Кількісний аналіз	Birubilin	Бірубілін
Complete analysis	Повний аналіз	Product yield	Вихід продукту реакції
Ultimate Analysis	Елементний аналіз	Refractive index	Коефіцієнт заломлення
Partial Analysis	Частковий аналіз	Thermal conductivity	Термічна провідність
Copper vitriol	Мідний купорос	Scattering	Розсіяння

1.1. The nature of analytical chemistry

Analytical chemistry is the branch of chemistry dealing with the separation and analysis of chemical substances. Traditionally, analysis has been concerned largely with chemical *composition*, but it is coming more and more to include the determination of chemical *structure* and the measurement of physical properties. Analytical chemistry includes both qualitative and quantitative analysis. Qualitative analysis is concerned with *what* is present, quantitative analysis - with *how much*, exclusively with the analysis of inorganic materials. Nevertheless, analytical chemistry properly includes the analysis of organic material too. Analytical chemistry finds extensive application in the analysis of organic compounds, fertilizers, pesticides, agrochemicals, plants, soils, pharmaceuticals, biochemicals, body fluids, hair, the atmosphere, polluted water, foods, alloys, and in many other areas.

1.2. What information does chemical analysis provide?

Qualitative analysis may be used to indicate the presence or absence of certain elements, ions, or molecules.

The most important aspect of analysis is still quantitative analysis, which provides data regarding the chemical composition of matter. These data may be quite detailed, or may be incomplete and general. The types of quantitative analysis may be classified as follows:

- *Complete analysis*. The amount of each constituent of the sample is determined quantitatively. For example, a complete analysis of a soil sample would tell the percentage of each compound present (pH, humus, ammonium nitrogen, nitrate nitrogen, nitrite nitrogen, amide nitrogen, organic nitrogen, inorganic phosphorus, potassium, calcium carbonate, iron oxide, heavy metals, alum silicates, etc). In many samples, such analysis would be a waste of time; instead a “complete” analysis is run for a select number of species. For example, in clinical laboratories, a “complete” blood analysis may involve the determination of eight or twelve species: glucose, Na^+, K^+, birubilin, alkaline phosphates, etc.

- *Ultimate Analysis*. The amount of each element in the sample is determined without regard to the actual compounds or ions present. An ultimate analysis of a gasoline sample would tell the percentage of carbon, hydrogen, oxygen, lead, phosphorus, etc.
- *Partial Analysis*. The amount of a certain selected constituent in a sample is determined. A partial analysis of copper vitriol might tell the percentage of copper (II). In the routine assay of commercial aspirin tablets, usually the amount of salicylic acid impurity gives the best indication of purity. Often a partial analysis will provide all of the information needed.

Where is Analytical chemistry used? The need for quantitative analysis is widespread - not only in chemistry, but also in commerce and in other fields of science, technology and agriculture. Some of the most important are:

Relating Chemical Composition to Physical Properties. The efficiency of a catalyst, the mechanical properties of a metal, the performance of a fuel, etc., may depend largely on chemical composition.

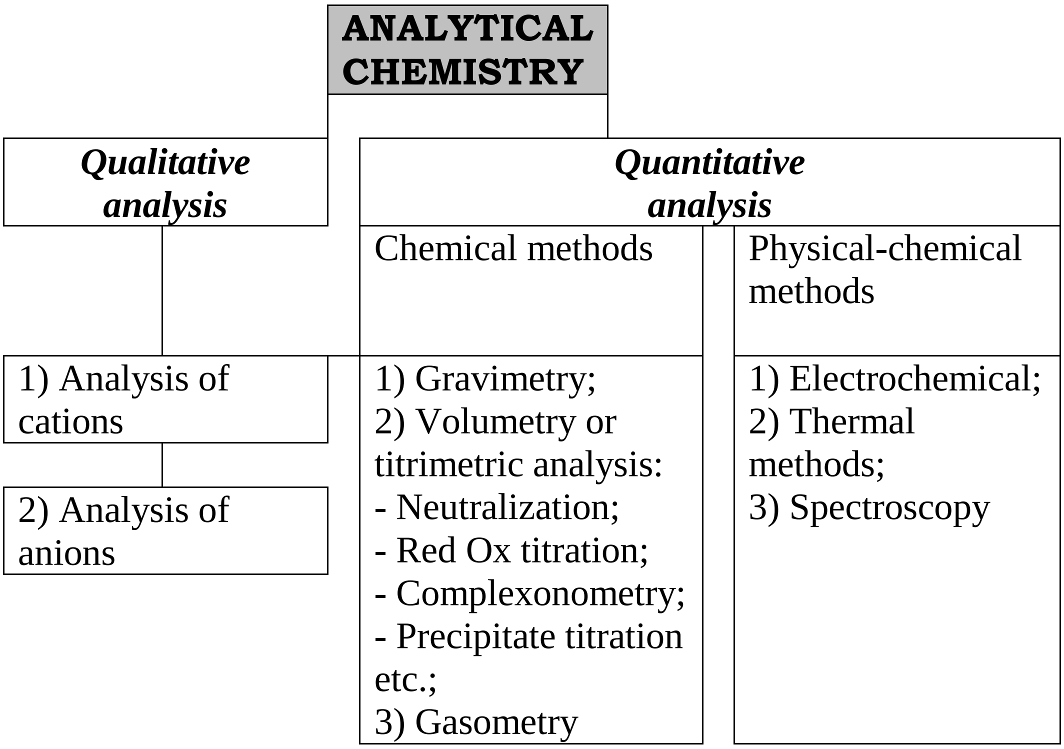
Quality Control. Chemical analysis is vital in maintaining good quality in the air we breathe and the water we drink. Standards must be set and frequent analyses performed to see that they are met. In industry, analysis in needed to see that raw materials meet specifications and to check the purity of the final product.

Determination the Amount of a Valuable Constituent. The determination of the amount of butterfat in cream, the amount of uranium in an ore, and the protein content of food are only few of many examples.

Diagnosis. Chemical analysis in finding increasing use in diagnosing disease. For example, the presence of a measurable amount of birubilin and more than 12 mg% of alkaline phosphatase (an enzyme) in a patient’s blood serum is indicative of an impaired liver function.

Research. Analytical chemistry is of major importance in connection with many research projects. Some examples are determining traces of metal that pass into solution (corrosion studies), finding out about a competitor's product, analyzing reaction mixtures to see which reaction conditions give the best product yield, and measuring extraction distribution ratios to find the best conditions for a large-scale extraction process.

What Methods Are Used in Quantitative Analysis? Methods of quantitative analysis are based on chemical reactions, on the measurement of certain chemical or physical properties (such as spectra), or of a combination of chemical and physical properties (photometric titration, for example). In some areas of analysis, instrumental methods based largely on the measurement of some physical property have preempted other analytical methods. Instrumental methods are often fast. For instance, a special emission spectrograph analyzes metal samples for several constituents in a few minutes.



In practice, quantifying analysis in a complex sample becomes an exercise in problem solving. To be effective and efficient, analyzing samples requires expertise in:

-the chemistry that can occur in a sample;

-analysis and sample handling methods for a wide variety of problems (the tools-of-the-trade);

-proper data analysis and record keeping.

To meet these needs, Analytical Chemistry courses usually emphasize chemical equilibrium, spectroscopic and electrochemical analysis, separations, and statistics.

Analytical chemistry requires broad background knowledge of chemical and physical concepts.

Methods of Detecting Analytes:

1. Physical means:
    - Mass;
    - Color;
    - Refractive index;
    - Thermal conductivity;
2. With electromagnetic radiation (Spectroscopy):
    - Absorption;
    - Emission;
    - Scattering;
3. By an electric charge:
    - Electrochemistry;
    - Mass spectrometry.

As you can see there are a limited number of ways to detect an analyte. However, in each of the above general categories there are a large multitude of specific analytical techniques.

CHAPTER 2. ANALYTICAL TECHNIQUES

Vocabulary

English	Українська назва	English	Українська назва
Semimicro Techniques	Напівмікроаналіз	Decant (pour off)	Декантувати (обережно зливати маточний прозорий розчин над осадом)
Dropwise	Дозувати реактиви (по краплям)		
DW	Дистильована вода		
Centrifuging	Центрифугування	Supernatant liquid	Маточний розчин
Evaporating	Випаровування		
Swirl	Воронка, лійка	Spatula	Шпатель
Stirring Rod	Паличка для перемішування розчинів	Porcelain casserole or evaporating dish	Фарфорова чашка чи чашка для випаровування
Wire gauze	Металева сітка (використовується для рівномірного розподілу полум'я газової горілки)	Balance pan	Чашка терезів
Slurry	Каламуть	Four places after the decimal	Чотири знаки після коми (точність зважування на аналітичних терезах)
Muffle furnace	Муфельна піч, муфель		
Meniscus	Меніск (рівень рідини у тонких трубках - піпетках, бюретках, мірних колбах)		

2.1. Semimicro Techniques

Proper performance of qualitative analysis requires knowledge of certain basic laboratory techniques. In order to speed up procedures, all techniques will be on a semimicro scale. This scale involves volumes of 1-2 mL of solutions and addes reagents dropwise with eye droppers. Containers are generally standard test tubes, which hold about 3 mL. Techniques for working with volumes of this magnitude will be outlined below:

- Water;
- Dispensing Reagent Solutions;
- Adjusting pH;
- Precipitation;
- Centrifuging;
- Washing a Precipitate;

- Transferring a Precipitate;
- Heating of Solution;
- Evaporating a Solution;
- Spatulas;
- Cleaning Glassware.

Water

Whenever it is necessary to use water in a procedure, use DW (DW). Ordinary tap water is not completely pure and may introduce substances, which you are trying to test, or it may introduce incompatible contamination.

Dispensing Reagent Solutions

When obtaining reagents from the reagent bottles, dispense always the reagent with the dropper contained in the reagent bottle, whether dispensing the reagent directly into your sample, or obtaining a quantity of reagent in another container.

Do not touch the dropper to the solution to which you add the reagent or to your sample container. Do not set the dropper on the reagent bench or lab bench. Return the stopper promptly to the reagent bottle from which it was originated. Do not place anything into a reagent bottle other than the dropper, which is contained in it. If you need a volume greater than 2 mL, use a graduated cylinder. For lesser volumes, if you want to calibrate one of eye droppers by counting how many drops of water it takes to deliver 1 mL into a graduated cylinder.

Stirring Rods

When reagents are added to a solution, it is essential that the solution be stirred thoroughly. Stirring rods can be prepared by cutting short lengths of thin glass rod and fire-polishing the ends.

The stirring rods get wet with each usage, and if not properly cleaned, will contaminate the next solution. A simple way to keep stirring rods clean is to place them in a beaker of clean DW and swirl them about after each use. The contamination will be highly diluted and can remain in the water. It is advisable to change the water periodically to minimize contamination.

Adjusting pH

At times you will want to make a solution acidic or basic. Add the proper reagent dropwise, stirring well with a stirring rod after each addition, and test the pH at appropriate intervals by touching the tip of the stirring rod to litmus or other pH indicating paper. Continue this procedure until the paper turns the proper color. If litmus paper is not sufficiently sensitive, obtain some pH indicator paper, which is available for various ranges of the pH scale.

Precipitation

In order to detect the formation of a precipitate, both the solution being used and the reagent must be clear (transparent, but not necessarily colorless). Precipitation is accomplished by adding the specified amount of reagent to the solution and stirring well. Stir both in a circular direction up and down. When precipitation appears to be complete, centrifuge to separate the solid. Before removing the supernatant liquid with a dropper or by decanting (pouring off), add a few drops more of the reagent to check for complete precipitation. If more precipitation occurs, add a few more drops of reagent, centrifuge, and test again.

Centrifuging

A centrifuge (Fig. 1) is used to separate a precipitate from a liquid. Put the test tube containing the precipitate into one of the locations in the centrifuge. Place another test tube containing an equal volume of water in the centrifuge location directly opposite your first test tube. This procedure is extremely important; it must be followed to maintain proper balance in the centrifuge. Otherwise, the centrifuge will not function properly and may be damaged.

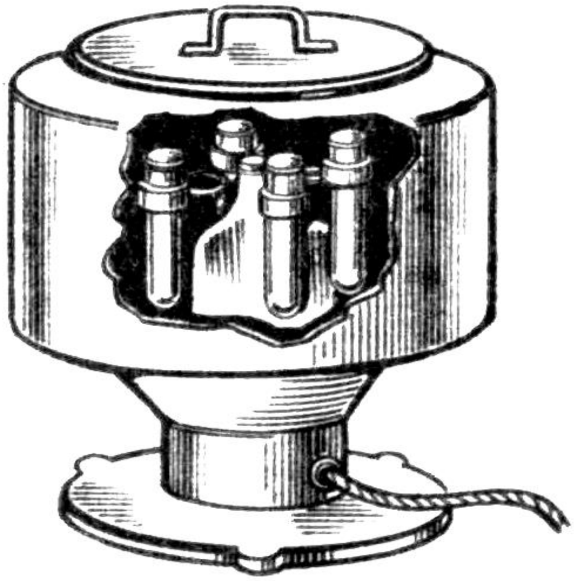


Figure 1 - Electrical centrifuge

Turn on the centrifuge and let it run for at least 30 seconds. Turn the centrifuge off and let it come to a complete stop without touching it. Stopping the centrifuge with your hand is not only dangerous, but is likely to stir up your precipitate. The precipitate should settle to a compact mass at the bottom of the test tube. The liquid above the precipitate (the supernatant) should not have any precipitate suspended in it. If it does, centrifuge again. The supernatant can then be poured off (decanted) into another test tube without disturbing the precipitate. All the liquid should be decanted in a single pouring motion to avoid re-suspending the precipitate. An eye dropper or a dropper with an elongated tip may also be used to draw off the supernatant.

Washing a Precipitate

After a precipitate has been centrifuged and the supernatant liquid decanted or drawn off, there is still a little liquid presented in the precipitate. To remove any ions, which might interfere with further testing, this liquid should be removed with wash liquid, usually DW. The wash liquid must be a substance, which will not interfere with the analysis, cause further precipitation, or dissolve the precipitate. Add the wash liquid to the precipitate, stir well, centrifuge, and decant the wash liquid. The wash liquid is usually discarded. Precipitates should be washed twice for best results.

Transferring a Precipitate

Sometimes you will want to divide a separated and washed precipitate into two portions, in order to carry out two additional tests. To transfer part of the precipitate to another test tube, add a small amount of DW to the precipitate, stir the mixture to form slurry, and quickly pour half of the slurry into another container. Do not use a spatula. This could contaminate your sample.

Heating Solutions

Test tubes containing reactions mixtures are never to be heated directly over an open flame. If a solution is to be heated, it should be placed in a test tube and suspended in a beaker of boiling (or in some cases only hot) water. It will be convenient to keep a beaker of water hot throughout the laboratory period. If hot water is required in a procedure, it should be DW heated in a test tube suspended in the beaker of boiling water. Do not use water directly from the beaker it may be contaminated.

Evaporating a Solution

Sometimes it is necessary to boil a solution to reduce the volume and concentrate a species or drive off a volatile species. To boil a liquid, place it in small porcelain casserole or evaporating dish and heat it on wire gauze with a small flame. Watch it carefully and do not overheat it. Generally, if you do not want to heat to dryness as this might decompose the sample. Stir the solution during the evaporation. Do not try to evaporate a solution in a small test tube. It will take much longer and the contents of the tube may be ejected if the tube is heated too strongly.

Spatulas

Never place a metal spatula in a solution. It may be dissolved and cause contamination. If you need to manipulate a solid, use a rubber policeman on a stirring rod.

Cleaning Glassware

Cleanliness is essential for a successful procedure. All apparatus must be cleaned well with soap and a brush, rinsed with tap water, and finally rinsed with DW (see below Chapter 2.4. Laboratory glassware cleaning procedures).

2.2. Analytical Techniques

For any piece of analytical equipment and glassware to provide precise and accurate results proper use and technique is essential. The purpose of this manual is to review this equipment and the necessary techniques.

Using Analytical Balances (Fig. 2):

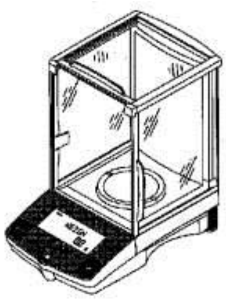


Figure 2 - Analytical Balance

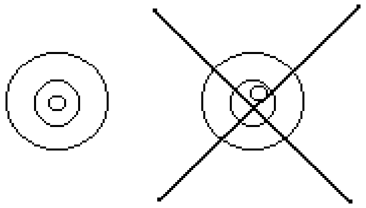


Figure 3 - Horizontal-level bubble gauge

Steps to be followed in Weighing by Addition:

1. Check to ensure that the horizontal position of the balance is leveled. Each balance is equipped with a level indicator (see Fig. 3). If the balance is not leveled see instruction.

2. Clean the balance pan with a brush.

3. Place a weighing boat, small beaker may also be used, on the center of the balance pan and be sure to close the balance doors.

4. Tare the balance and wait until it reads zero grams.

5. Remove the weigh boat from the balance. Gently add solid sample to the weighing boat. Never add reagent while the weigh boat is in the balance!!!

6. Return the weigh boat to the balance and close the balance door. Record the weight to the nearest tenth of a milligram, i.e., four places after the decimal.

7. Remove the boat and sample. Transfer the sample to the appropriate piece of glassware.

Steps to be followed in Weighing by Difference:

This technique is useful when several duplicate masses of a material must be weighed out.

1. Check to ensure that the horizontal position of the balance is leveled. Each balance is equipped with a level indicator (see Fig. 3). If it is not leveled see instruction.

2. Clean the balance pan with a brush.

3. Place a weighing boat on the centre of the balance pan and be sure to close the balance doors.

4. Tare the balance and wait until it reads zero grams.

5. Remove the weigh boat from the balance. Place approximately 1-4 grams of the material to be measured into the weighing boat. Never add reagent while the weigh boat is in the balance!!!

6. Return the weigh boat to the balance and close the balance door. Record the weight to the nearest tenth of a milligram, i.e., four places after the decimal.

7. Carefully remove some material from the weigh boat and place it in an appropriate container. Reweigh the weigh boat. The difference between the original weight and the final weight is equal to the weight of sample taken. Repeat if necessary.

Be sure to avoid the following common mistakes when using either the analytical or trip balance (where applicable):

a) Handling weighing bottles with bare fingers;
b) Weighing damp or dirty objects;
c) Leaving balance doors open;
d) Leaving weights on the balance when finished;
e) Forgetting to turn off the balance;
f) Removing the object from the pan while the balance is still on;
g) Weighing an object, which is above room temperature.

2.3. Analytical Glassware

In many laboratory experiments small amounts of reagents must be dispensed not only very accurately but also with a great deal of precision. In analytical experiments precise amounts of reagents are dispensed using glassware diagrammed in Fig. 4.

Graduated cylinders are the least precise of the analytical glassware but are suitable for most applications and the easiness of use makes them a valuable piece of analytical glassware.

Pipets and burets must be kept absolutely clean in order to retain proper calibration. It is good practice in general to see that all glassware is absolutely clean. To test for cleanliness, fill the object with water and then empty it. If the remaining water forms a uniform thin film on the walls with no beads, the object is clean.

Clean burets rinse repeatedly with DW. Special type of burets has a Teflon bore stopcock: loosen the buret nut slightly to prevent freezing during storage.

Pipets and burets with hard-to-remove residues must be cleaned using soap and water. A buret brush may be used for cleaning a buret. Take care not to scratch the insides of the buret. Rinse well with DW after cleaning or use. Always rinse pipets well with DW after use and store them flat.

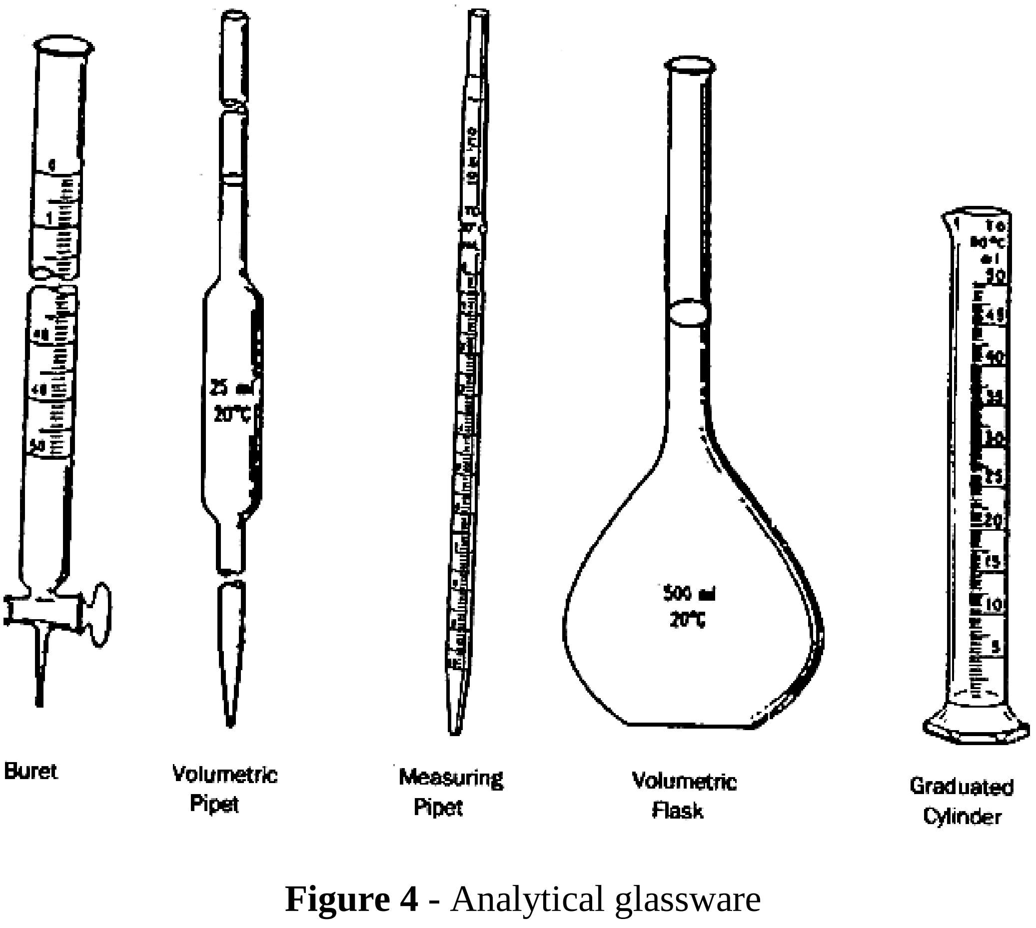


Figure 4 - Analytical glassware

Use of Pipets:

Pipets are calibrated to deliver (TD) a measured volume of a liquid. Two types are commonly used in chemistry laboratories: volumetric (or transfer) pipets and measuring pipets (see Fig. 5, 6).

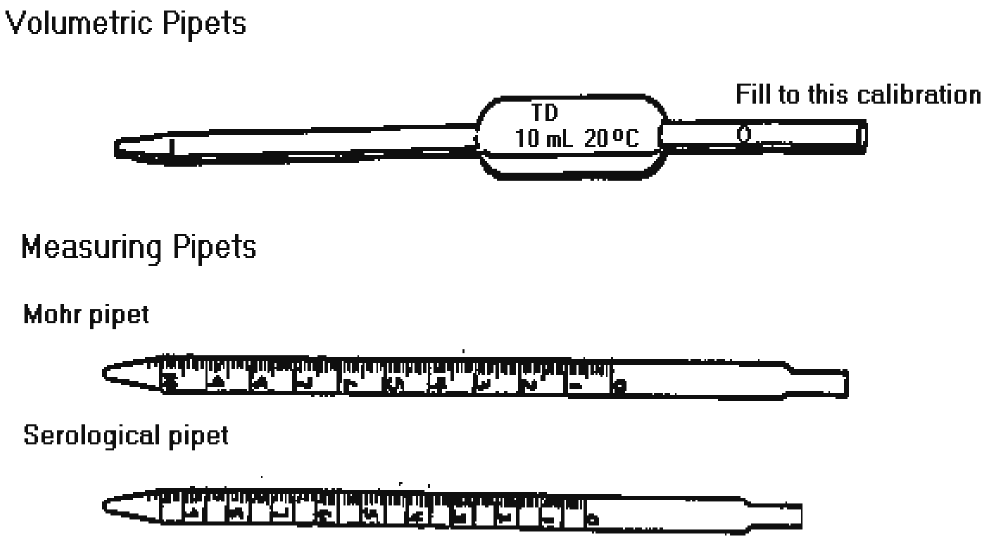


Figure 5 - Types of pipets

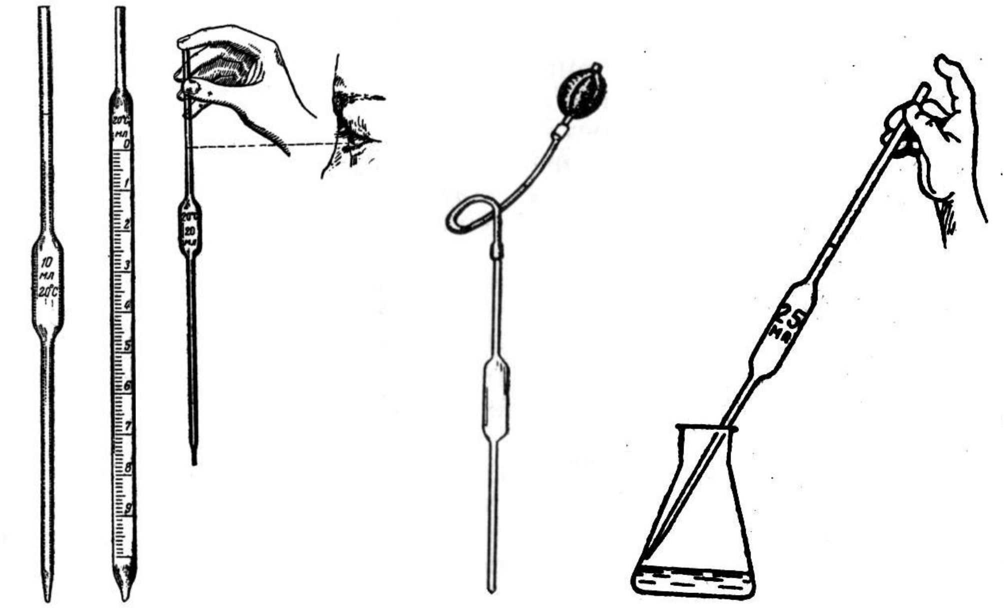


Figure 6 - Using of Volumetric and Measuring pipets

As the above diagram shows, a volumetric pipet has one calibration mark and is designed to deliver one fixed volume. Various capacities (i.e. 5 mL, 20 mL, 50 mL etc.) are available and are accurate to two digits after the decimal. The pipet shown above is calibrated to deliver exactly 10 mL at 20°C and should be recorded as 10.00 mL.

Measuring pipets include Serological and Mohr pipets. They deliver various volumes to varying degrees of accuracy. The measuring pipet is calibrated along its length: either straight to the tip or along the straight part of the pipet only. These pipets are usually not as accurate as volumetric pipets. Both measuring pipets shown above are calibrated as "10 in 1/10" which means the pipet delivers a maximum of 10 mL and is calibrated in 0,1 mL divisions. Volume measurements should be recorded to two digits after the decimal.

The Mohr pipet is calibrated to deliver to the 10 mL baseline. The tip cannot be allowed to drain. The Serological pipet is usually calibrated to deliver the tip.

1. Squeeze the air out of the pipet bulb and press the opening of the bulb against the opening of the pipet. Do not push the pipet into the bulb. The tip of the pipet must be kept under the surface of the liquid during suction is applied or air will be sucked into the pipet.

2. Rinse the pipet well with at least two portions of the desired solution.

3. Fill the pipet above the calibration mark using a pipet bulb.

4. Quickly remove the bulb and place your index finger (not your thumb) over the end of the pipet.

5. Wipe the pipet tip clean of any excess solution.

6. Drain the solution in the pipet down to the calibration mark by gently reducing the pressure of your index finger. You do not have to remove your index finger. Tip the pipet against the beaker to remove any excess solution. If your finger "leaks" and allows the level in the pipet to drop below the calibration line, moisten your finger slightly and try again.

7. Reset the pipet tip against the wall of the container into which the solution is to be transferred and allow the solution to drain. Volumetric pipets are allowed to drain completely. Measuring pipets should not be allowed to go past the desired volume levels. Leave the pipet in this position for at least 10 seconds after all the solution appears to have drained out and touch the pipet tip to the side of the flask to remove any droplets. Remove the pipet. DO NOT BLOW OUT THE SOLUTION REMAINING IN THE PIPET!!!

8. Rinse the pipet well with DW and store it when finished.

Use of Volumetric Flasks:

Volumetric flasks (Fig. 7) are available with capacities ranging from 5 to 5000 mL. They are normally calibrated to contain (TC) a specified volume at 20°C. The volumetric shown below is calibrated to contain exactly 250 mL at 20°C and should be recorded as 250,00 mL.

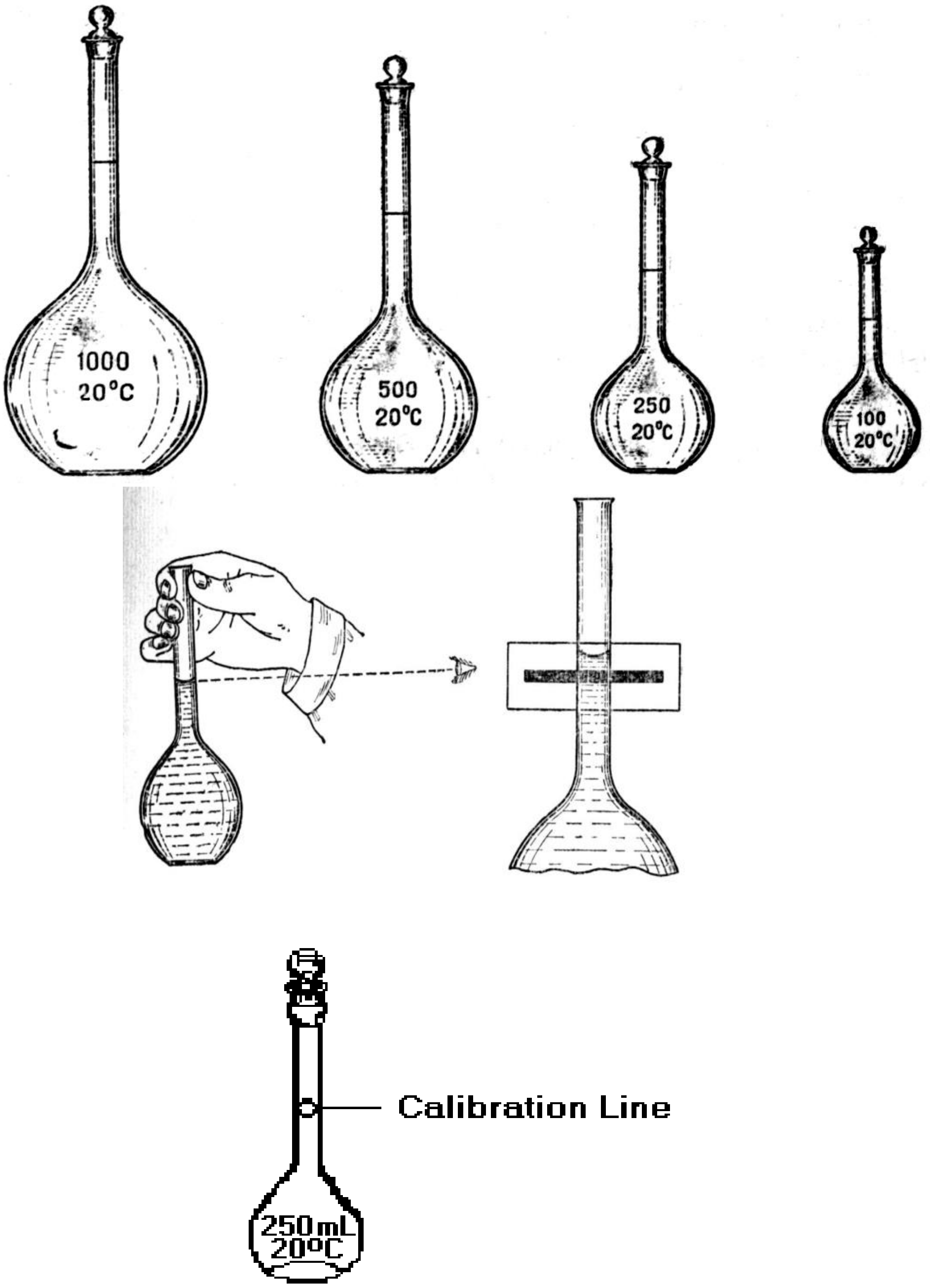


Figure 7 - Volumetric flasks and their using

The calibration mark is a ring around the narrow neck of the flask. A volumetric flask is used for making a solution whose concentration must be exactly known.

Some volumetric flasks have two calibration marks, TC and TD. The TD mark is above the TC mark and includes the amount of solution that remains on the wall of the flask when emptied. All TD volumetric ware is calibrated to take into account the film of solution that remains on the vessel walls. This is the reason that correct calibration is maintained only with clean glassware.

Volumetric flasks are properly filled when the bottom of the solution meniscus is exactly at the calibration mark. Always read or adjust the solution level in your glassware with your eye exactly leveled with the meniscus. This avoids a parallax error. On your buret use the calibration marks that completely encircle the buret to estimate when your eye is leveled with the meniscus. Estimation of the meniscus bottom can be aided by placing a white card with a black line drawn horizontally across it behind the glassware and bringing the black line up to the meniscus.

1. Solid reagent (the solute) is transferred to the volumetric flask by using a funnel. The weighing boat is rinsed with the solvent used (usually DW) into the funnel. Then the funnel is rinsed with solvent while still inserted in the flask so that any remaining solute particles will be washed into the flask. In this way, the solute is transferred quantitatively - nothing is left behind.

2. After the solute has been added, the flask should be filled about halfway, and then swirled until all the solute has dissolved. Then solvent is added near to the calibration mark but not up to it.

3. Final addition is accomplished using a medicine dropper. If the liquid level goes past the calibration mark the solution must be discarded. Make sure your eyes are leveled with the liquid surface, and add solvent drop-wise until the bottom of the meniscus is touching the calibration line. It is important that the solution is well mixed. Stopper and invert the flask several times.

When using a volumetric flask to prepare a solution from a solid or pure liquid, it is usually best to weigh the desired substance by difference to an ordinary beaker. Dissolve the substance in the beaker with pure solvent (usually DW) being careful not to splash any solution out of the beaker. Transfer this solution to the volumetric flask quantitatively using a funnel. To avoid any solution running down the outside of the beaker, place a stirring rod across the top of the beaker. This rod should be fitted into the pouring depression on the beaker and extended about 1 cm beyond the lip. Use this rod to guide the solution into the flask. Rinse the beaker three times with solvent and transfer these rinses to the flask in the same manner. Fill the flask at least 95% full by adding solvent and mix thoroughly. Add enough solvent carefully and slowly to bring the solution level with the calibration mark using a medicine dropper for the last few drops. Again shake well to mix thoroughly. Never dilute to the mark if the solution temperature differs significantly from room temperature.

Use of Burets:

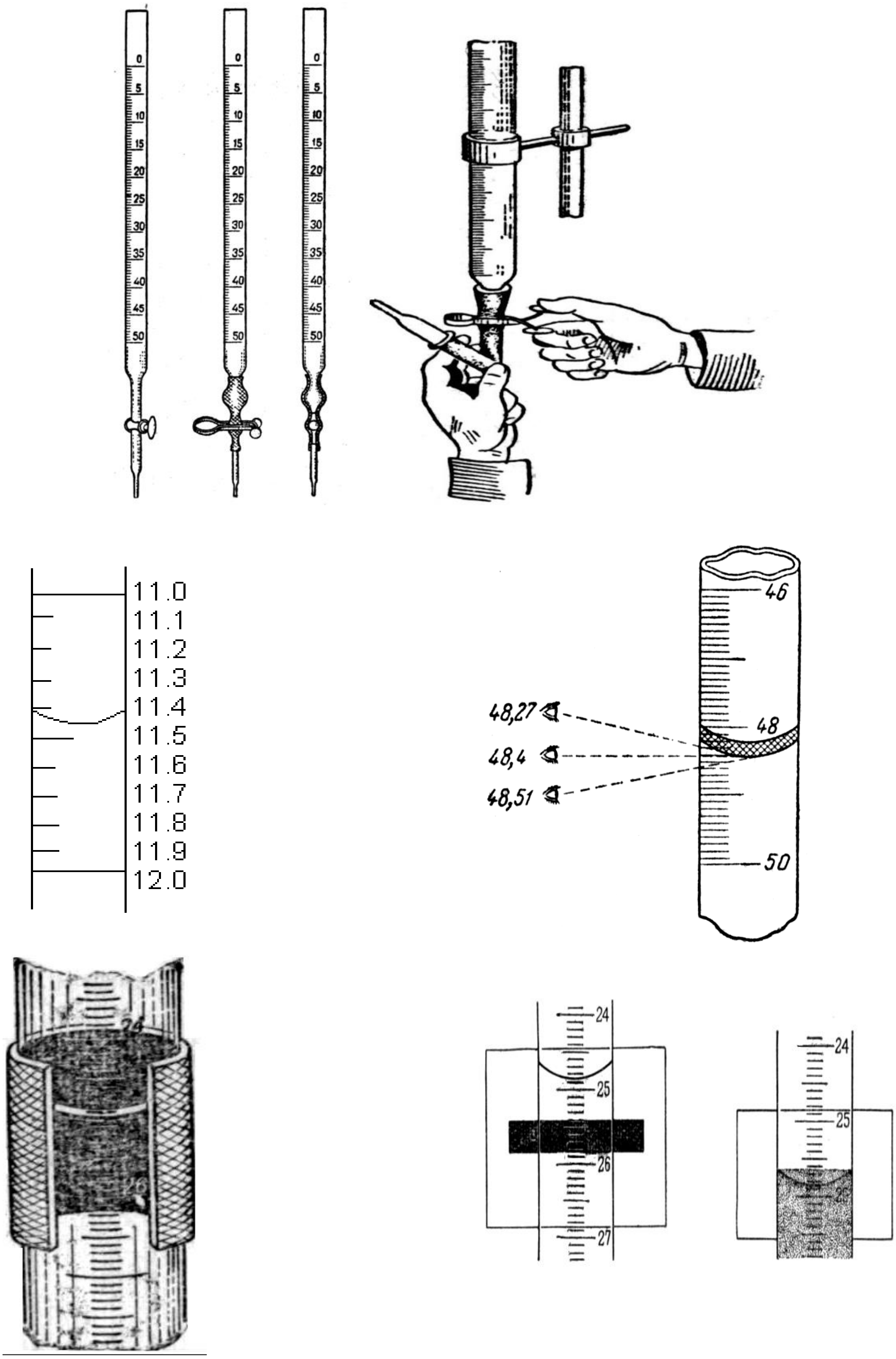


Figure 8 - Diagram of a buret and it’s using

A buret is a glass tube with graduations that can be used to determine the volume of a solution added to a receiving vessel.

A buret is calibrated to be read from the top down. For example, a 25 mL buret will have the zero mark at the top and 25 mL mark at the bottom, above the stopcock. To determine the volume dispensed from the buret, use the graduation that is closest to the lowest point of the meniscus. As an example, in the diagram, the meniscus is between the 11,4 and 11,5 mL marks. Thus the column of liquid dispensed would be recorded as 11,45 mL, assuming that the titration was begun at zero.

Using a buret is not difficult; however, good technique is needed to titrate accurately (Fig. 8).

1. Be sure the buret is clean by rinsing several times with DW. Drain the buret well and rinse at least twice with the desired solution and discard the washings.

2. Fill the buret and drain to or below the 0,00 mL mark.

3. After a suitable time for drainage along the walls, wipe any excess solution from the buret tip and be sure that no air bubbles are trapped in either the tip or on the sides of the buret. If air bubbles are present in the tip, open the stopcock completely to force them out. If there are air bubbles on the sides of the buret, gently tap the buret to get them to rise to the surface. Read the buret to 2 places after the decimal.

4. Deliver the required amount of solution and read the buret again. If you have emptied the buret rapidly, wait for the solution on the walls to drain before making a reading.

5. During titrations the titrant, solution in the buret, should be added slowly to the titrated solution. A flow rate of 1-2 drops per second is recommended. It is essential that the titrant be mixed thoroughly with the solution being titrated throughout the titration. Be sure to stir or swirl the solution into which the titrant is being added to insure complete mixing of the constituents.

6. When approaching the end point of a titration with a color change that is not sharp, note down the volume and color after each addition to avoid overrunning the endpoint. Approach the end point of all titrations with extreme care. After each addition contact the buret tip with the wall of the titration vessel to remove any drop of titrant remaining on the tip and be sure to wash down the sides of the receiving vessel.

7. Always estimate the buret reading to 0,1 mL.

8. When finished, rinse the buret well with DW.

2.4. Laboratory glassware cleaning procedures

In the analysis of samples the preparation of scrupulously clean glassware is mandatory. Lab glassware cleaning procedures must follow specific written method requirements. If procedures are not listed then the method of cleaning should be adapted to both the substances that are to be removed, and the determinations (tests) to be performed. Recommendations for such cleaning procedures are listed below.

Lab Glassware Cleaning Procedures

Analysis/Parameter	Cleaning Procedure (In order specified)
ORGANICS	
Semi-Volatile:	
(Pesticides, Herbicides, Oil & Grease)	Solvents: 5, 1-4, 5 or 6, 13, 15 or Muffle: 5, 1-4, 12, 13, 15 Or Oxidizer: 5, 1-3, 14,
INORGANICS	
Trace Metals:	1-4, 9, 8 (optional), 4
Nutrients, Minerals:	1-4, 8, 4
Solids:	1-4, 11 (Volatile Solids 16)
Non-Metals, Physical Properties: (Cyanide)	1-4, 14
MICROBIOLOGY	1-4, (Sterilize per approved method)
Analysis/Parameter	Cleaning Procedure (In order specified)
BIOASSAY	
Freshwater:	18, 2, 3, 9 or 8, 4, 5, 4, 20
Marine & Estuarine:	19, 2, 3, 9 or 8, 4, 5, 4, 20
RADIONUCLIDES	17, 3, 8, 4

Cleaning Procedures:

1. Remove all labels using sponge or acetone.

2. Wash with hot tap water and a brush to scrub inside of glassware, stopcocks, and other small pieces, if possible, using a suitable laboratory-grade detergent. Organics - Liquinox, Alconox or equivalents.

Inorganic anions - Liquinox or equivalent.

Inorganic cations - Liquinox, Acationox, Micro or equivalents.

Microbiology- must pass inhibitory residue test.

3. Rinse thoroughly with hot tap water.
4. Rinse thoroughly with deionized water.
5. Rinse thoroughly with pesticide grade Acetone.
6. Rinse thoroughly with pesticide grade Methanol.
7. Rinse thoroughly with pesticide grade Hexane.
8. Rinse or soak with 1:1 HCl (Hydrochloric Acid).
9. Rinse or soak with >10% HNO_3 (Nitrate Acid).
10. Bake at 105°C for 1 hour.
11. Bake at 180°C (prior to use as per method).
12. Drain, then heat in muffle furnace for 30-60 minutes at 400°C.
13. Clean, dry glassware should be sealed and stored in dust-free environment.
14. Soak in oxidizing agent (Chromic acid or equivalent); preferably hot (40-50°C).
15. Last step (prior to use) should be a rinse with the solvent used in analysis.
16. Drain, then heat in muffle furnace for 1 hour at 550°C.
17. Heat 1 hour in EDTA solution at 90-100°C.
18. New glassware must be soaked overnight in 10% HNO_3 or HCl.
19. New glassware must be soaked overnight in seawater.
20. Rinse thoroughly with DW.

2.5. Analytical purity of chemicals

Analyts offer chemicals of large diversity in grading and types of use summarized as follows:

Technical grade

These products are suitable for non-critical examined mixtures in the laboratory such as rinsing, dissolving or are used as raw materials in production examined mixtures.

Synthesis reagents

Those reagents which are suitable for organic synthesis and preparative applications.

Extra Pure grade

This quality is associated to products that are suitable for qualitative and semi-quantitative grades. These chemicals suitable for general laboratory works, and in most cases, meet Most Pharmacopoeia Standards (BP, USP etc.).

Pharmacopoeia Grade

Products and solutions meeting the purity requirements of chemical products admitted in the pharmaceutical sector (pharmacopoeia requirement such as NF, BP, USP, Ph Eur, DAB, DAC, JP, and Ph Franc.)

For Analytical Purpose

This quality is suitable for most analytical application, research and quality control.

Guaranteed Reagent (GR)

It is the ideal quality for laboratory purposes. Batch to batch reproducibility is specially controlled to guarantee consistent analytical results. The grade is equivalent to Analytical grade (A.R.) Reagent grade (R.G.), p.a. nomenclature of other manufacturers.

ACS reagent

Reagents meet the specification of American Chemical Society (ACS) Analytical reagents found in most laboratories and are used in a wide variety of analytical techniques for quality control, research and development.

HPLC reagent

Product range is specially made for high performance liquid chromatography (HPLC). Within this range there are different qualities depending on whether they will be used for preparative chromatography or analytical in isocratic or gradient mode. The range includes high purity solvents, tested to meet strict UV absorbance specifications as well as ion pair reagents.

Ion Pair Reagents

Ion pair chromatography is done when the analytes of interest include ionic compounds that are difficult to separate by reverse phase chromatography. Ion pair reagents are added to the mobile phase and combine with ionic analytes. The neutral compounds formed can be chromatography by reverse phase HPLC. We offer both cationic and anionic ion pair reagents in special HPLC grade qualities to assure trouble-free separations.

Pesticide & GC residue

Solvents are specially tested to avoid organic impurities at ppt levels. These solvents are specially purified in a multi-step process using only glassware equipment. Inert conditions are kept during bottling to assure optimum performance and to avoid any possibility of contamination.

Dry & Anhydrous

Solvents with very low water content, applicable for analytical purposses or organic synthesis. Dry solvents are traditionally used in water determinations according to Karl Fischer and anhydrous solvents are becoming more necessary in the new organic and inorganic chemistry research techniques. In our catalogue, you can also find extra-dry grade solvent or extra-dry with molecular sieves.

Peptide and DNA synthesis

The most important features of these products are low UV absorption and low water content.

Spectroscopy grade

Solvents display a high UV permeability and are subject to strict IR Spectroscopy tests.

Food/ FCC grade

Products meet the strength specifications and maximum impurity limit indicated in the Food Chemicals Codex (FCC).

Molecular biology reagents

These products are specially controlled to guarantee the absence of enzymes that could interfere in the analysis and an adequate transparency for the detection techniques used in molecular biology.

Biotech/ Biochemistry grade

Highly pure reagents suitable for biochemical research and analysis. The critical parameters involved are absence of inhibitors such as traces of heavy metals as well as biochemical function tests for enzymes, coenzymes and enzyme substrates.

Microbiology grade

We offer hundreds microbiological products with some dehydrated culture media auxiliary agent and other manual systems in its range.

Fluorescence grade

Our fluorescence HPLC grade is gradient and fluorescence controlled. It is specially suitable for PAH analysis by HPLC.

For Microscopy

We offer various types of chemicals and reagents for microscopy use.

GPC reagent

Specially stabilized Tetrahydrofuran is available for GPC (gel permeation chromatography). This THF can be used for column-storage, since it does not form damaging peroxides.

Cell Culture grade

Cell culture reagents include cell culture media, laboratory preparations, biological extracts, selective and sterile reagents for several applications.

ProteomicsProteomics defined as the qualitative and quantitative comparison of proteomes under different conditions to further unravel biological processes; we offer reagents for this usage.

Histology grade

We offer solvents and reagents purity meets the histological uses.

Ultra pure grade

Ultra pure reagents are used in inorganic trace analysis where impurities must be low in the ppt or ppb level. Each reagent is delivered complete with a lot analysis certificate.

Electronic/ VLSI/ ULSI/ SLSI grade

Reagents used for semiconductor industry, cations, anions and particles value guarantee to ppm to ppb level. Our range of chemicals covers all products required in cleaning and etching processes for semiconductor production.

ASTM products

In the analysis of oil derivatives it is of interest that the reagents and apparatus are manufactured under the American Society of Testing and Materials guidelines.

Acids with low mercury content

These acids are used in environmental analysis when analyzing traces of mercury, and assure that no interferences are added to the samples because of the acids.

AA and ICP standard solutions 1000 ppm

They are made out of high-purity salts and acids, or bases. The accuracy of its concentration is checked by using titrimetric and gravimetric methods. These solutions can be used in atomic absorption spectroscopy, polarography or colorimetric techniques. They are traceable to NIST with certificate.

Volumetric solutions

Ready to use volumetric solutions and most of them are traceable to NIST.

pH buffer solution

We offer a broad range of ready to use buffer solutions for pH-meter calibration. They are accurate and traceable to NIST. Colored solution of pH 4, 7, 10 available for easy differentiation.

Karl Fischer reagent

Karl Fischer titration is widely used to quantify water content in many different samples. It is used both in industrial processes and in quality control laboratories. Our KF reagents are pyridine-free, which contain non toxic imidzole. It has a good buffer capacity and allows fast and stable titration end-points

2.6. Calculating Concentration: Units & Dilutions

Chemists use the term solute to describe the substance of interest and the term solvent to describe the material in which the solute is dissolved. For example, in a can of soda pop (a solution of sugar in carbonated water), there are approximately twelve tablespoons of sugar (the solute) dissolved in the carbonated water (the solvent). In general, the component that is present in the greatest amount is termed the solvent. The concentration of a chemical solution refers to the amount of solute that is dissolved in a solvent. We normally think of a solute as a solid that is added to a solvent (e.g., adding table salt to water), but the solute could just as easily exist in another phase. For example, if we add a small amount of ethanol to water, then the ethanol is the solute and the water is the solvent. If we add a smaller amount of water to a larger amount of ethanol, then the water could be the solute.

Often in informal, non-technical language, concentration is described in a qualitative way, through the use of adjectives such as "dilute" or "weak" for solutions of relatively low concentration and of others like "concentrated" or "strong" for solutions of relatively high concentration. Those terms relate the amount of a substance in a mixture to the observable intensity of effects or properties caused by that substance. For example, a practical rule is that that the more concentrated a chromatic solution is, the more intensely colored it is. The concentration of a chemical substance expresses the amount of a substance present in a mixture. There are many different ways to express concentration.

Qualitative Description

These glasses (Fig. 9) containing red dye demonstrate qualitative changes in concentration. The solutions on the left are more dilute, compared to the more concentrated solutions on the right.

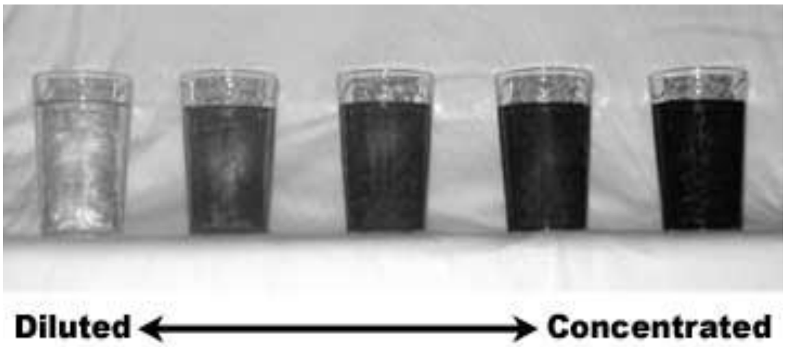


Figure 9 - Qualitative description of concentration change

Quantitative Description: Units of Concentration

Concentration may be expressed by several different ways, using percent composition by mass, mole fraction, molarity, molarity, normality, titr.

1. Percent Composition by Mass (mass concentration, percent concentration) (P, %)

This is the mass of the solute divided by the mass of the solution (mass of solute plus mass of solvent), multiplied by 100.

Or: the number of grams of solute dissolved in 100 g of solution. For example, the percent composition of a solution made from 10 g of Sodium Hydroxide (NaOH) dissolved in 90 g of water is found as follows:

$$P = \frac{\text{Mass of solute } m_s}{\text{mass of solute } m_s + \text{mass of solvent } m_{solv}} \times 100\% \qquad \textbf{(1)}$$

$$P = \frac{10\text{ g NaOH}}{10\text{ g NaOH} + 90\text{ g } H_2O} \times 100\% = 10\,\%\text{ NaOH (by mass)}.$$

Note that the mass of solution is the sum of the masses of the solute and solvent. Percent concentration is common for solutions used for practical purposes - household or industrial cleaning, killing pests in the garden, medical applications. Percent-by-mass concentration is based only on the mass of solute and is unrelated to its chemical formula of molar mass.

$$P = \frac{m_{solute}}{m_{solution}} \times 100\% \qquad (2)$$

Example:

Determine the percent composition by mass of a 100 g salt solution, which contains 20 g salt.

Solution: 20 g NaCl/100 g solution x 100 = 20% NaCl solution.

Mass can be determined at a precision of < 0.2 mg on a routine basis with an analytical balance and more precise instruments exist. Both solids and liquids are easily quantified by weighing. The volume of a liquid is usually determined by calibrated glassware such as burettes and volumetric flasks.

For very small volumes precision syringes are available. The use of graduated beakers and cylinders is not recommended as their indication of volume is mostly for decorative rather than quantitative purposes. The volume of solids, particularly of powders, is often difficult to measure, which is why mass is the more usual measure. For gases the opposite is true, the volume of a gas can be measured in a gas burette, if care is taken to control the pressure. The mass is not so easy to measure due to buoyancy effects.

2. Parts per million (ppm). Parts per million works like percent by mass, but is more convenient when there is only a small amount of solute present. PPM is defined as the mass of the component in solution divided by the total mass of the solution multiplied by 10^6 (one million):

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \cdot 1000000 \qquad (3)$$

Solution with a concentration of 1 ppm has 1 gram of substance for every million grams of solution. Because the density of water is 1 g per mL and we add such a tiny amount of solute, the density of a solution at such a low concentration is approximately 1 g per mL. Therefore, in general, one ppm implies one milligram of solute per liter of solution. Finally, recognize that one percent = 10 000 ppm. Therefore, something that has a concentration of 300 ppm could also be said to have a concentration of (300 ppm)/(10,000 ppm/percent) = 0,03% percent by mass.

3. Parts per billion (ppb). This works like above, but we multiply by one billion (10^9; caution: the word billion has different meanings in different countries). A solution with 1 ppb of solute has 1 microgram (10^{-6} g) of material per liter.

4. Parts per trillion (ppt). This works like parts per million and parts per billion except that we multiply by one trillion (10^{12}). There are few, if any, solutes which are harmful at concentrations as low as 1 ppt. **Note:** "ppt" is sometimes used as laboratory shorthand for precipitate, which is entirely unrelated.

5. Molarity (molar concentration) (M)

Molarity (M) is the number of moles of solute in one liter of solution. To find the molarity of a solution one must know the molar mass of the solute.

For example, “one-molar” solution of Sodium hydroxide (NaOH) contains one mole of NaOH in each liter of solution. The concentration of the proceeding solution is written as 1 M NaOH.

One mole of Sodium hydroxide (NaOH) has a mass of 40 g/mol. This quantity of NaOH dissolved in enough amount of water to make exactly 1,00 L of solution gives a 1 M solution. If 20,0 g of NaOH, which is 0,500 mol, is dissolved in 1,00 L of solution, 0,500 M NaOH solution is produced:

$$\textbf{Molarity} = \frac{Number\ of\ moles\ of\ solute}{Number\ of\ Litres\ of\ Solution} = \frac{\nu}{V} = \frac{0{,}500\,\mathrm{mol\ NaOH}}{1{,}00\,\mathrm{L}} =$$

= 0,500 M NaOH.

So, one molar solution is not made by adding 1 mol of solute to 1 L of solvent. In such case, the final total volume would be slightly different from 1 L. Instead of this 1 mol of salute is firstly dissolved in less than 1 L of solvent. Then, the resulting solution is carefully diluted with more solvent to bring the total volume to 1 L, using volumetric flask (Fig. 5).

Molarity is useful when the quantity of solute participating in a chemical reaction taking place in solution is of interest. Any required molar quantity of the solute can be selected by measuring out the appropriate volume of the solution of known molarity.

$$\mathrm{M} = \frac{\nu}{V} = \frac{mass\ of\ solute}{Molar\ mass\ of\ solute \times Volume\ of\ solution\ in\ litres} \quad \text{or}$$

$$\boldsymbol{M = \frac{m_{solute}}{M_{solute} \times V}} \qquad (4)$$

Although molarity is by far the most commonly used measure for concentration, particularly for dilute aqueous solutions, it does suffer from a number of disadvantages. Masses can be determined with great precision as balances are often very precise. Determining volume is often not as precise. In addition, a volume of a liquid changes with temperature so that the molarity also changes without adding or removing any mass. For non-dilute solutions another problem is that the molar volume of a substance is itself a function of concentration so that volume is not strictly additive.

6. Mole Fraction (X)

This is the number of moles of a compound divided by the total number of moles of all chemical species in the solution. Keep in mind, the sum of all mole fractions in a solution is always equal to 1.

Example:

What is the mole fractions of the components of the solution formed when 92 g of glycerol is mixed with 90 g of water? (Molecular mass water = 18 g/mol; molecular mass of glycerol = 92 g/mol).

Solution:

90 g of water = 90 g x 1 mol / 18 g = 5 mol of water;

92 g of glycerol = 92 g x 1 mol / 92 g = 1 mol of glycerol;

Total mol = 5 + 1 = 6 mol;

x_{water} = 5 mol /6 mol = 0,833;

$x_{glycerol}$ = 1 mol /6 mol = 0,167.

It's a good idea to check your math by making sure the mole fractions add up to 1:

$x_{water} + x_{glycerol} = 0{,}833 + 0{,}167 = 1{,}000$.

7. Molality (m)

Molality is the number of moles of solute per kilogram of solvent. Because the density of water at 25°C is about 1 kilogram per liter, molality is approximately equal to molarity for dilute aqueous solutions at this temperature. These is a useful approximation, but remember that it is only an approximation and doesn't apply when the solution is at a different temperature, isn't dilute, or uses a solvent other than water.

Example:

What is the molality of a solution of 10 g of NaOH in 500 g of water?

Solution:

10 g of NaOH / (4 g of NaOH/1 mol NaOH) = 0,25 mol of NaOH.

500 g of water x 1 kg / 1000 g = 0,50 kg of water.

Molality = 0,25 mol/ 0,50 kg =0,05 M/kg = 0,50 m.

8. Normality (normal concentration)

Normality is equal to the *gram equivalent mass* of a solute per liter of solution. A gram equivalent mass or equivalent is a measure of the reactive capacity of a given molecule.

The concentration of solutions can be expressed by stating the quantity of the solute in equivalents rather than in moles. This measure of concentration is called Normality (N). The normality of solution is the number of equivalents (υ_E) of solute per liter (V) of solution:

$$\textbf{Normality} = \frac{\text{Number of equivalents of solute}}{\text{Number of Litres of Solution}} = \frac{\nu_E}{V}. \qquad (5)$$

The normality of an acid or base solution is commonly expressed using the number of H^+ or OH^- ions available for a complete neutralization. Therefore:

$$E_{acid} = \frac{M_{acid}}{\text{number of hydrogen atoms in acid}},$$

$$E_{base} = \frac{M_{base}}{\text{number of OH groups in base}}.$$

For neutral salts equivalent mass may be expressed as:

$$E_{neutral\ salt} = \frac{M_{neutral\ salt}}{\text{number of atoms of metals in salt} \times \text{Valency of metals}},$$

where

E_{acid}, E_{base}, $E_{neutral\ salt}$ - equivalent mass of acid, base or neutral salt respectively, g/g-eq;

M_{acid}, M_{base}, $M_{neutral\ salt}$ - molar mass of acid, base or neutral salt respectively, g/mol.

So, $v_E = \frac{m_{solute}}{E_{solute}}$ and

$$N = \frac{m_{solute}}{E_{solute} \times V} \qquad (6)$$

Example:

1 M sulfate acid (H_2SO_4) is 2 N for acid-base reactions because each mole of sulfate aicid provides 2 moles of H^+ ions. On the other hand, 1 M sulfate acid is 1 N for sulfate precipitation, since 1 mole of sulfate acid provides 1 mole of sulfate ions.

9. Titr

Titr (T) is a special unit for measuring of concentration connected with chemical quantitative analysis. Titr is the number of grams of solute in 1 milliliter of solution. For example, the titr of a solution made from 0,3 g of Silver Nitrate ($AgNO_3$) dissolved in 150 mL of solution is found as follows:

$$T = \frac{\text{Mass of solute } m_S \text{ in grams}}{\text{Volume of solution in mililiters}} =$$

$$= \frac{0{,}3\,\text{g AgNO}_3}{1150\ \text{mL of soution}} = 0{,}002\ \text{g/mL}.$$

$$\text{So, } T = \frac{m_{solute\ in\ g}}{V_{solution\ in\ mL}} \qquad (7)$$

Dilutions

Process of solution diluting consists in adding of a solvent to a solution. Adding solvent results in a solution of lower concentration. It can calculate the concentration of a solution following a dilution by applying this equation:

$$M_iV_i = M_fV_f \text{ or } N_iV_i = N_fV_f$$

where M is molarity, N - normality, V is volume, and the subscripts i and f refer to the initial and final values.

Example:

How many milliliters of 5,5 M NaOH are needed to prepare 300 mL of 1,2 M NaOH?

Solution:

5,5 M x V_1 = 1,2M x 0,3 L;

V_1=1,2 M x 0,3 L/5,5 M;

V_1=0,065 L = 65 mL.

So, to prepare the 1,2 M NaOH solution, you pour 65 mL of 5,5 M NaOH into your container and add water to get 300 mL of final volume.

Conversion of units’ concentration is presented in Table 1.

Table 1. Units of concentration and formulas for their recalculation

Units of concentration	Recalculation formulas			
	M	N	T	P
M, mol/L	-	$\frac{N \cdot E_{solute}}{M_{solute}}$	$\frac{T \cdot 1000}{M_{solute}}$	$\frac{P \cdot 10\,d}{M_{solute}}$
N, g-eq/L	$\frac{M \cdot M_{solute}}{E}$	-	$\frac{T \cdot 1000}{E_{solute}}$	$\frac{P \cdot 10d}{E_{solute}}$
T, g/mL	$\frac{M \cdot M_{solute}}{1000}$	$\frac{N \cdot E_{solute}}{1000}$	-	$\frac{P \cdot d}{100}$
P, ω, % (by mass)	$\frac{M \cdot M_{solute}}{10d}$	$\frac{N \cdot E_{solute}}{10d}$	$\frac{T \cdot 100}{d}$	-

Notes: E_{solute} –equivalent mass of solute (g/g-eq); M_{solute} – molar mass of solute (g/mol); d – density of solution, g/cm^3.

In atmospheric chemistry and in air pollution regulations, the parts per notation is commonly expressed with a **v** following, such as **ppmv**, to indicate parts per million by volume. This works fine for gas concentrations (e.g., ppmv of carbon dioxide in the ambient air) but, for concentrations of non-gaseous substances such as aerosols, cloud droplets, and particulate matter in the ambient air, the concentrations are commonly expressed as $\mu g/m^3$ or mg/m^3 (e.g., μg or mg of particulates per cubic meter of ambient air). This expression eliminates the need to take into account the impact of temperature and pressure on the density and hence weight of the gas. The usage is generally quite fixed inside most specific branches of science, leading some researchers to believe that their own usage (mass/mass, volume/volume or others) is the only correct one. This, in turn, leads them not to specify their usage in their research, and others may therefore misinterpret their results. For example, electrochemists often use volume/volume, while chemical engineers may use mass/mass as well as volume/volume. Many academic papers of otherwise excellent level fail to specify their usage of the part-per notation. The difference between expressing concentrations as mass/mass or volume/volume is quite significant when dealing with gases and it is very important to specify which is being used. It is quite simple, for example, to distinguish ppm by volume from ppm by mass or weight by using **ppmv** or **ppmw.**

PROBLEMS:

1. To calculate a percent concentration of solution of nitrate acid, which contains 460 g of water and 40 g of HNO_3.
2. How many grams of Chile saltpeter (sodium nitrate, M ($NaNO_3$) = 85 g/mol) are contained in 2 L of 0,05 N solution of this salt?
3. To calculate molar concentration of 2 N solution of sulfate acid (M (H_2SO_4) = 98 g/mol).
4. How many grams of Potassium hydroxide KOH is needed to weight for preparation of 250 mL of solution with titr 0,01 g/mL?
5. To calculate normal concentration of 10% solution of $CaCl_2$ (M ($CaCl_2$ = 111 g/mol), density ρ = 1,083 g/cm^3.
6. To calculate percent concentration of 2 M solution of Sodium Sulfate (M (Na_2SO_4) = 142 g/mol), density of solution ρ = 1,02 g/cm^3.

CHAPTER 3. QUALITATIVE ANALYSIS

Vocabulary

English	**Українська назва**	**English**	**Українська назва**
Analytical кeagent	Аналітичний реагент	Nessler's reagent	Реактив Несслера
Group reagent	Груповий реагент	Red blood salt	Червона кров'яна сіль
Specific reagent	Специфічний реагент	Yellow blood salt	Жовта кров'яна сіль
Selective reagent	Селективний реагент	Turnbull's blue	Турнбулева синь
Sensitivity	Чутливість (аналітичної реакції)	Prussian blue	Пруська (берлінська) лазур
Detectable minimum	Визначуваний мінімум	Carbonic gas	Вуглекислий газ
Concentration limit	Мінімальна концентрація	Molybdenum liquid	Молібденова рідина
Maximum dilution	Максимальне розбавлення	Magnesia mixture	Магнезіальна суміш

3.1. General ideas

The aim of qualitative analysis is to determine the chemical elements of substance to be analyzed, ions, atom or molecule groups which are in its composition.

Determination of elements or ions, which are part of investigated substance, can be carried out using different methods: chemical, physical, and physical-chemical. Unlike covalent compounds, which can be identified using physical properties like boiling point and refractive index, ionic compounds are more appropriately identified with their chemical properties.

In the qualitative analysis procedure, the chemical properties of an unknown substance are determined by systematically reacting the unknown with a number of different reagents. By predetermining what the particular reaction will produce if a specific ion is present, the ions that actually are in the solution can be identified. For example, if a reaction is known to produce a precipitate if ion A is present and a precipitate is formed when the reaction is run, then ion A may be present in solution (there may be, and usually are, other ions that will also precipitate with a particular reagent). If no precipitate is formed when the reaction is run, then ion A is clearly not present in the unknown solution and a different reaction will have to be run to determine what ions are present.

There are two general situations in which qualitative analysis is used - in the identification of a simple salt, or the identification of multiple cations in a solution.

Using chemical method the analyzed substance is transformed into new compound having characteristic properties: color, odor, and defined physical state. Chemical transformation which takes place is called qualitative analytical reaction and the substances initiated this transformation are called **analytical reagents.**

Group reagents react with the group of ions and provide the same effect; **specific reagents** react with only one ion; **selective reagents** react with two or three ions.

Analytical reactions to be carried out are mostly influenced by the following:

1) pH;
2) Ion concentration;
3) Temperature.

The sensitivity of the reaction is determined by the following:

1) Detectable minimum;
2) Minimum concentration;
3) Maximum dilution.

Detectible minimum (m) is the less quantity of substance or ion, which can be detected by given reaction at certain conditions. It is expressed in $\gamma = 10^{-6}$ g.

Concentration limit (c) is the minimum concentration of determined ion in solution at which the analytical reaction gives positive effect. Concentration limit is expressed as the ratio of substance mass (1 g) to solution volume (in mL). For example, for qualitative determination of Cu^{2+} by reaction with water solution of ammonia $NH_3 \cdot H_2O$ minimum concentration is equal to 1: 250 000. It means that 1 g of Cu^{2+} may be detected in 250 liters of analyzing solution.

Detectable minimum and concentration limit are interrelated:

$$m = c \cdot V \cdot 10;$$

$$c = m/V \cdot 10^6;$$

Where V - volume of solution, mL.

Maximum dilution (MD) is an index inverse to minimum concentration: MD = 1/c. Maximum dilution indicates at which solution volume 1 g of the substance should be presented in order the reaction to be visible. So the sensitivity of reaction is higher if maximum dilution is bigger and detectable minimum and minimum concentration is smaller.

3.2. Qualitative analysis of cations

Qualitative analysis is used to separate and detect cations and anions in a sample substance. In an educational setting, it is generally true that the concentrations of the ions to be identified are all approximately 0.01 M in an aqueous solution. The semimicro technique of qualitative analysis employs methods used to detect 1-2 mg of an ion in 5 mL of solution.

First, ions are removed in groups from the initial aqueous solution. After each group has been separated, then testing is conducted for the individual ions in each group. There are several types of classifications.

Many reagents are used in qualitative analysis, but only a few are involved in nearly every group procedure. The four most commonly used reagents are 6M HCl, 6M HNO_3, 6M NaOH, 6M NH_3. Understanding the use of the reagents is helpful when planning an analysis (Table 2).

Table 2. Common Qualitative Analysis Reagents

Reagent	Effects
6M HCl	Increases $[H^+]$; Increases $[Cl^-]$; Decreases $[OH^-]$; Dissolves insoluble carbonates, chromates, hydroxides, some sulfates; Destroys hydroxo and NH_3 complexes; Precipitates insoluble chlorides.
6M HNO_3	Increases $[H^+]$; Decreases $[OH^-]$; Dissolves insoluble carbonates, chromates, and hydroxides; Destroys hydroxo and ammonia complexes; Good oxidizing agent when hot.
6M NaOH	Increases $[OH^-]$ Decreases $[H^+]$ Forms hydroxo complexes Precipitates insoluble hydroxides.
6M NH_3	Increases $[NH_3]$; Increases $[OH^-]$; Decreases $[H^+]$; Precipitates insoluble hydroxides; Forms NH_3 complexes; Forms a basic buffer with NH_4^+.

Among the most common reactions in qualitative analysis are those involving the formation or decomposition of complex ions and precipitation reactions. These reactions may be performed directly by adding the appropriate anion, or a reagent such as H_2S or NH_3 may dissociate in water to furnish the anion. Strong acid may be used to dissolve precipitates containing a basic anion. Ammonia or sodium hydroxide may be used to bring a solid into solution if the cation in the precipitate forms a stable complex with NH_3 or OH^- (Table 3).

Table 3. Complexes of Cations with NH_3 and OH^-

Cation	NH_3 Complex	OH^- Complex
Ag^+	$[Ag(NH_3)_2]^+$	-
Pb^{2+}	-	$[Pb(OH)_4]^{2-}$
Al^{3+}	-	$[Al(OH)_4]^-$
Cu^{2+}	$[Cu(NH_3)_4]^{2+}$ (dark blue)	-
Zn^{2+}	$[Zn(NH_3)_4]^{2+}$	$[Zn(OH)_4]^{2-}$
Co^{2+}	$[Co(NH_3)_6]^{2+}$ (lilac)	-
Ni^{2+}	$[Ni(NH_3)_6]^{2+}$ (blue)	-

A cation is usually presented as a single principal species, which may be a complex ion, free ion, or precipitate. If the reaction goes to completion the principal species is a complex ion. The precipitate is the principal species if most of the precipitate remains undissolved. If a cation forms a stable complex, addition of a complexing agent at 1M or greater generally will convert the free ion to complex ion. For the purpose of qualitative analysis, cations are classified into groups on the basis of their behavior against some reagents. By the systematic use of these group reagents we can decide if there is presence or absence of groups of cations, and can also separate these groups for further examination.

The group reagents used for classification of most common cations are hydrochloric acid HCl, hydrogen sulphide H_2S, ammonium sulfide $(NH_4)_2S$, ammonium carbonate $(NH_4)_2CO_3$ - so-called sulphide classification - classical method of chemical analysis (Table 4). The other ions are soluble hydrochloric acid HCl, sulfate acid H_2SO_4, Caustic Soda NaOH and ammonia $NH_3{\cdot}H_2O$ (so-called acid-base classification - see Table 5). The most secure method of classification is based on using of ammonium or sodium phosphates and called amino-phosphate classification (see Table 6). This method was elaborated for examination of cations K^+, Na^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Sn^{2+}, Sn^{4+}, Sb^{3+}, Sb^{5+}, As^{3+}, As^{5+}, Ag^+, Hg^{2+}, Pb^{2+}. Ammonia-phosphate classification of cations is based on the difference in solubility of phosphates in water, weak and strong acids, alkalis and ammonia.

Agricultural practice is connected with using of the next common biologically active cations:

macronutrients: NH_4^+, Ca^{2+}, K^+, Na^+, Mg^{2+}, Al^{3+}; micronutrients: Mn^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Fe^{2+}, Fe^{3+};

cations of toxic and radioactive elements: Sr^{2+}, Cu^{2+}, Ag^+, Cr^{3+}, Ba^{2+}, Hg^{2+}, Pb^{2+}.

Table 4. Principles of sulphide classification of cations

Groups of cations	I	II	III		IV		V
			A	B	A	B	
Characteristics of group	Sulphides and carbonates are soluble in water	Sulphides are soluble in water; Carbonates are insoluble in water	Sulphides or formed on their basis hydroxides due to hydrolysis are soluble in diluted acids		Sulphides are insoluble in diluted acids		
			Hydroxides are amphoteric	Hydroxides are not amphoteric	Sulphides are insoluble in Na_2S solution	Sulphides are soluble in Na_2S solution	Chlorides are insoluble in water
Cations	Na^+, K^+, NH_4^+	Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}	Al^{3+}, Cr^{3+}, Zn^{2+}	Fe^{2+}, Fe^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}	Cu^{2+}, Bi^{3+}, Cd^{2+}	As (III, V), Sb (III, V), Sn^{2+}, Sn (IV), Hg^{2+}	Ag^+, Hg_2^{2+}, Pb^{2+}
Group reagent	no	$(NH_4)_2CO_3$	$(NH_4)_2S$ in presence NH_4OH and NH_4Cl		H_2S in presence HCl		HCl

Table 5. Principles of acid-base classification of cations

Group	Cations	Group reagent	Properties of sediments			
			Solubility in:			
			H_2O	$NH_3 \cdot H_2O$	HCl, HNO_3	NaOH
1	NH_4^+, Na^+, K^+	No	-	-	-	-
2	Ag^+, Pb^{2+}	HCl	Insoluble in water ($PbCl_2$ soluble in boiling H_2O)	$[Ag(NH_3)_2]Cl$ solution	Insoluble in water	$Na_2[Pb(OH)_4]$ solution
3	Ca^{2+}, Sr^{2+}, Ba^{2+}	H_2SO_4 (diluted, 20%)	Insoluble in water	$(NH_4)_2[Ca(SO_4)_2]$ solution	Insoluble in water	Insoluble in water
4	Al^{3+}, Zn^{2+}	NaOH	Insoluble in water	$[Me^{n+}(NH_3)_{2n}]^{n+}$ solution	Soluble in water	Soluble in water
5	Mg^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}	NaOH (excess)	Insoluble in water	Insoluble in water	Soluble in water	Insoluble in water
6	Cu^{2+}, Co^{2+}, Ni^{2+}	$NH_3 \cdot H_2O$	Insoluble in water	$[Me^{n+}(NH_3)_{2n}]^{n+}$	Soluble in water	Insoluble in water

Table 6. Principles of amino-phosphate classification of cations

Group		Cations	Group reagent	Properties of sediments				
				Solubility in:				
				H_2O	$NH_3 \cdot H_2O$	CH_3COOH	HCl, HNO_3	NaOH
1		NH_4^+, Na^+, K^+	-	-	-	-	-	-
2	A	Mg^{2+}, Mn^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Fe^{2+}	$(NH_4)_2HPO_4$ + $NH_3 \cdot H_2O$	Insoluble in water	Insoluble in water	Soluble in water	Soluble in water	Insoluble in water
	B	Fe^{3+}, Al^{3+}				Insoluble in water		$Na_3[Al(OH)_6]$ solution
3		Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}	$(NH_4)_2HPO_4$ or Na_2HPO_4	Insoluble in water	$[Me^{n+}(NH_3)_{(2-3)n}]^{n+}$	Soluble in water	Soluble in water	$Na_2[Zn(OH)_4]$ solution
4		Ag^+, Pb^{2+}	HCl	Insoluble ($PbCl_2$ soluble in boiling H_2O)	$[Ag(NH_3)_2]Cl$	Insoluble in water	Insoluble in water	$Na_2[Pb(OH)_4]$ solution

3.3. The first group of cations

3.3.1. Characteristic reactions of ammonia cations NH_4^+

1. Alkalis (*NaOH, KOH*). Alkalis isolate ammonia from ammonia salts at heating:

$$NH_4^+ + OH^- = NH_3 + H_2O$$

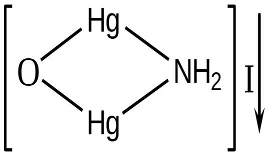
$$NH_4Cl + NaOH \xrightarrow{t} NH_3\uparrow + NaCl + H_2O.$$

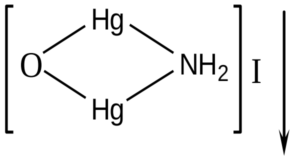
Reaction is highly sensitive, specific; concentration limit c=1:5000000.

Test carrying out

Add 4-5 drops of NaOH or KOH solution to 3-4 drops of ammonia salt and heat at water bath. Isolated ammonia is detected on odor or red litmus paper wetted by DW, which becomes blue in ammonia vapor.

2. Nessler's reagent *$K_2[HgI_4]$+KOH* forms red-brown precipitation with ammonia ions:

$NH_4^+ + 2[HgI_4]^{2-} + 4KOH =$  $+ 7 I^- + 3H_2O;$

$NH_4Cl + 2K_2[HgI_4] + 4KOH =$  $+ 7KI + KCl + 3H_2O.$

Test carrying out

Add 2-3 drops of Nessler's reagent to 1-2 drops of diluted ammonia salt. In presence of ammonia ion trace the solution becomes orange.

Reaction is highly sensitive, concentration limit c = 1:10000000.

3.3.2. Characteristic reactions of Potassium cations K^+

1. Potassium hexanitritocobaltate (III) *$Na_3[Co(NO_2)_6]$* isolates yellow crystalline precipitation of double salt of potassium and sodium from K^+ salt solution:

$$2 K^+ + Na^+ + [Co(NO_2)_6]^{3-} = K_2Na[Co(NO_2)_6]\downarrow$$

$$2 KCl + Na_3[Co(NO_2)_6] = K_2Na[Co(NO_2)_6]\downarrow + 2NaCl.$$

Test carrying out

Add 3-4 drops of reagent to 2-3 drops of potassium salt solution.

Analyzed solution should have pH not more than 7 because reagent is easily destroyed in alkali medium:

$$Na_3[Co(NO_2)_6] + 3NaOH = Co(OH)_3\downarrow + 6NaNO_2.$$

At pH less than 7 unstable acid is formed:

$$K_2Na[Co(NO_2)_6]\downarrow + 3HCl = H_3[Co(NO_2)_6] \text{ (solution)} + NaCl + 2KCl;$$

$$2H_3[Co(NO_2)_6] + 4HCl = 5NO + 2CoCl_2 + 7NO_2 + 5H_2O.$$

Reagent and precipitation are not destroyed in acetic acid.

The ions of ammonia prevent the determination of Potassium ions, because ammonia forms the same yellow precipitation like potassium ions:

$$2NH_4Cl + Na_3[Co(NO_2)_6] = (NH_4)_2Na[Co(NO_2)_6]\downarrow + 2NaCl.$$

Concentration limit c = 1:13000.

2. Sodium hydrotartrate *$NaHC_4H_4O_6$* isolates white crystalline precipitation of potassium hydrotartrate from neutral solution. Reaction is low sensitive (concentration limit c = 1 : 1000):

$$K^+ + HC_4H_4O_6^- = KHC_4H_4O_6\downarrow$$

$$KCl + NaHC_4H_4O_6 = KHC_4H_4O_6\downarrow + NaCl.$$

Test carrying out

Add to 4-5 drops of K^+ salt solution the same volume of reagent. Condition of reaction realization:

pH = 5 to 7;

ammonia ions absence, because the same precipitation is formed:

$$NH_4Cl + NaHC_4H_4O_6 = NH_4HC_4H_4O_6\downarrow + NaCl;$$

Cooling;

Crystallization center formation (to rub by glass stick).

Concentration limit c = 1:1000.

3.3.3. Characteristic reactions of Sodium cations Na^+

1. Potassium hexahydroxostibiate *$K[Sb(OH)_6]$* forms white crystalline precipitation with sodium ions:

$$Na^+ + [Sb(OH)_6]^- = Na[Sb(OH)_6]\downarrow$$

$$NaCl + K[Sb(OH)_6] = Na[Sb(OH)_6]\downarrow + KCl.$$

Test carrying out

pH=5-7; The precipitation of $Na[Sb(OH)_6]$ is dissolved with the formation of Na_3SbO_4 in strong alkaline medium;

absence of ammonia ions because the ammonia salts are hydrolyzed taking acidic medium. Reactant $K[Sb(OH)_6]$ is decomposed forming precipitation of methastibic acid:

$$[Sb(OH)_6]^- + H^+ = HSbO_3 + 3H_2O,$$

cooling;

crystallization center formation (to rub by glass stick).

Concentration limit c=1:3300.

2. Zinc-Uranyl-Acetate *$Zn(UO_2)_3(CH_3COO)_8$* forms with sodium ions light green-yellow crystalline sediment of Sodium-Uranyl-Acetate $NaZn(UO_2)_3(CH_3COO)_9 \cdot 9H_2O$. Reaction is very sensitive (concentration limit c=1:11000000), specific. Ions of Na^+ are determined in presence of large excess (20-times and more) of other ions: NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Al^{3+}, Fe^{3+}, Sr^{2+}, Pb^{2+}, et al.:

$$Na^+ + Zn^{2+} + 3\,UO_2^{2+} + 8CH_3COO^- + CH_3COOH + 9H_2O =$$
$$= NaZn(UO_2)_3(CH_3COO)_9 \cdot 9H_2O\downarrow;$$

For example,

$$NaCl + Zn(UO_2)_3(CH_3COO)_8 + CH_3COOH + 9H_2O =$$
$$NaZn(UO_2)_3(CH_3COO)_9 \cdot 9H_2O\downarrow + HCl.$$

Test carrying out

pH=4-7 (Acetic acid medium);

Initialization of crystallization by rubbing of tube sides by glass stick.

Add 8-10 drops of Zinc-Uranyl-Acetate solution to 3-4 drops of sodium salt solution and rub of tube sides by glass stick. In presence of Na^+ ions it is precipitated light green-yellow crystalline sediment.

3.4. The third group of cations

3.4.1. Characteristic reactions of Copper cations Cu^{2+}

1. Group reagent *$(NH_4)_2HPO_4$* forms blue crystalline precipitation with copper ions:

$$3Cu^{2+} + 2HPO_4^{2-} + 2NH_4OH = Cu_3(PO_4)_2\downarrow + 2NH_4^+ + 2H_2O$$
$$3CuSO_4 + 2(NH_4)_2HPO_4 + 2NH_4OH = Cu_3(PO_4)_2\downarrow + 3(NH_4)_2SO_4 +$$
$$+ 2H_2O.$$

Test carrying out

Add to test-tube 10-12 drops of $(NH_4)_2HPO_4$, 4-6 drops of NH_4OH, 10-12 drops NH_4Cl and 10-12 drops of copper salt.

Copper phosphate is soluble in acetic, mineral acids and ammonia.

2. Water ammonia *NH_4OH*. The reaction is carried out in two stages:

the 1st: $2Cu^{2+} + SO_4^{2-} + 2NH_4OH = (CuOH)_2SO_4\downarrow + 2NH_4^+$;

the 2d: $(CuOH)_2SO_4 + 2NH_4^+ + 6NH_4OH = \underset{\text{solution}}{2[Cu(NH_3)_4]^{2+}} + 8H_2O$

For example,

$$2CuSO_4 + 2NH_4OH = (CuOH)_2SO_4\downarrow + (NH_4)_2SO_4;$$
$$(CuOH)_2SO_4\downarrow + (NH_4)_2SO_4 + 6NH_4OH = 2[Cu(NH_3)_4]SO_4 + 8H_2O.$$

Test carrying out

Add little by little NH_4OH solution to 3-4 drops of copper salt solution up to basic salt formation (precipitation) and then the excess of NH_4OH up to the dilution of precipitation and formation of complex compound which has dark blue color. This reaction is highly sensitive (c=1:500000).

3. Alkalis (*NaOH, KOH*). Alkali forms blue precipitation with copper ions:

$$Cu^{2+} + 2OH^- = Cu(OH)_2\downarrow$$

For example, in molecular form:

$$CuCl_2 + 2NaOH = Cu(OH)_2\downarrow + 2NaCl.$$

Copper hydroxide has weakly amphoteric properties, may be dissolved in mineral and acetic acids.

Test carrying out

Add 2-3 drops of NaOH or KOH to solution of copper salt to forming of blue precipitation.

4. Potassium ferricyanide *$K_4[Fe(CN)_6]$* *(yellow blood salt)* forms red-brown precipitation with copper ions (pH<7):

$$2Cu^{2+} + [Fe(CN)_6]^{4-} = Cu_2[Fe(CN)_6]\downarrow$$

For example, in molecular form:

$$2CuCl_2 + K_4[Fe(CN)_6] = Cu_2[Fe(CN)_6]\downarrow + 4KCl.$$

This reaction is highly sensitive (c=1:2500000).

Precipitation $Cu_2[Fe(CN)_6]$ is not dissolved in diluted acids, but is solved in excess of water ammonia.

Test carrying out

Add 1 drop of HCl and 2-3 drops of $K_4[Fe(CN)_6]$ to 3-4 drops of Copper salt solution.

5. Potassium Iodide *KI* reacts with copper salt formed white precipitation CuI. But reactive mass has brown-red color due to free I_2 isolation. This reaction is Red-Ox:

$$2Cu^{2+} + 4I^- \rightarrow 2CuI\downarrow + I_2.$$

For example, in molecular form:

$$2CuSO_4 + 4KI = 2CuI + I_2 + 2K_2SO_4$$

$$\begin{array}{l|l} 2I^- - 2e \rightarrow I_2 & 1 \\ Cu^{2+} + 1e \rightarrow Cu^+ & 2 \end{array}$$

Test carrying out

Add 2-3 drops of KI solution to 3-4 drops of Copper salt solution.

3.4.2. Characteristic reactions of Zinc cations Zn^{2+}

1. Group reagent *$(NH_4)_2HPO_4$* forms white crystalline precipitation with zinc ions:

$$3Zn^{2+} + 2HPO_4^{2-} + 2NH_4OH = Zn_3(PO_4)_2\downarrow + 2NH_4^+ + 2H_2O$$

$$3ZnSO_4 + 2(NH_4)_2HPO_4 + 2NH_4OH = Zn_3(PO_4)_2\downarrow + 3(NH_4)_2SO_4 + \\ + 2H_2O.$$

Test carrying out

Add to test-tube 10-12 drops of $(NH_4)_2HPO_4$, 4-6 drops of NH_4OH, 10-12 drops NH_4Cl and 10-12 drops of zinc salt.

Zinc phosphate is diluted in acetic, mineral acids, ammonia and in alkali excess.

2. Water ammonia *NH_4OH* forms white precipitation with Zn ions ($Zn(OH)_2$) which is diluted in excess of NH_4OH with the formation of complex compound:

$$Zn^{2+} + 2NH_4OH = Zn(OH)_2\downarrow + 2NH_4^+;$$

For example,

$$ZnCl_2 + 2NH_4OH = Zn(OH)_2\downarrow + 2NH_4Cl;$$

$$Zn(OH)_2 + 4NH_4OH \text{ (in excess)} = \underset{\text{colorless solution}}{[Zn(NH_3)_4](OH)_2} + 4H_2O.$$

Test carrying out

Add 2-3 drops of water ammonia to 2-3 drops of zinc salt solution to forming of white precipitation. Add excess of ammonia up to solving of precipitation.

3. Alkalis *(NaOH, KOH).* Sodium hydroxide forms white amorphous precipitation with Zn ions - $Zn(OH)_2$ which is the amphoteric hydroxide soluble in acid and alkali:

$$Zn^{2+} + 2OH^- = Zn(OH)_2;$$

$$Zn(OH)_2 + 2H^+ = Zn^{2+} + 2H_2O;$$

$$Zn(OH)_2 + 2OH^- = ZnO_2^{2-} + 2H_2O;$$

For example,

$$ZnCl_2 + 2NaOH = Zn(OH)_2\downarrow + 2NaCl;$$

$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O;$$

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O.$$

Test carrying out

Add slowly 10-12 drops of zinc salt solution to 2-3 drops of NaOH or KOH solution up to forming of white precipitation $Zn(OH)_2$.

4. Potassium ferrocyanide *$K_3[Fe(CN)_6]$* (red blood salt) forms precipitation of mustard color with Zn ions (pH<7):

$$3Zn^{2+} + 2[Fe(CN)_6]^{3-} = Zn_3[Fe(CN)_6]_2\downarrow;$$

For example,

$$3ZnCl_2 + 2K_3[Fe(CN)_6] = Zn_3[Fe(CN)_6]_2\downarrow + 6KCl.$$

Precipitation is solved in alkalis:

$$Zn_3[Fe(CN)_6]_2 + 18OH^- = 3ZnO_2^{2-} + 2Fe(OH)_3 + 12CN^- + 6H_2O.$$

Test carrying out

Add 1 drops HCl and 2-3 drops of $K_4[Fe(CN)_6]$ to 2-3 drops of zinc salt solution.

3.4.3. Characteristic reactions of Cobalt cations Co^{2+}

1. Group reagent *$(NH_4)_2HPO_4$* forms lilac crystalline precipitation with cobalt ions:

$$3Co^{2+} + 2HPO_4^{2-} + 2NH_4OH = Co_3(PO_4)_2\downarrow + 2NH_4^+ + 2H_2O$$

$$3CoCl_2 + 2(NH_4)_2HPO_4 + 2NH_4OH = Co_3(PO_4)_2\downarrow + 6NH_4Cl + \\ + 2H_2O.$$

Test carrying out

Add to test-tube 10-12 drops of $(NH_4)_2HPO_4$, 4-6 drops of NH_4OH, 10-12 drops NH_4Cl and 10-12 drops of cobalt salt.

Cobalt phosphate is diluted in acetic, mineral acids, ammonia.

2. Water ammonia *NH_4OH*. The reaction is carried out in two stages:

the 1st: $Co^{2+} + Cl^- + NH_4OH = \underset{\text{lilac}}{CoOHCl\downarrow} + NH_4^+;$

the 2d: $CoOHCl\downarrow + 7NH_4OH = \underset{\text{lilac solution}}{[Co(NH_3)_6]^{2+}} + 2OH^- + NH_4^+ + Cl^- + 6H_2O;$

For example,

$$CoCl_2 + NH_4OH = CoOHCl\downarrow + NH_4Cl;$$

$$CuOHCl\downarrow + 7NH_4OH = [Co(NH_3)_6](OH)_2 + NH_4Cl + 6H_2O.$$

Test carrying out

Add little by little NH_4OH solution to 3-4 drops of copper salt solution up to basic salt formation (precipitation) and then the excess of NH_4OH up to the dilution of precipitation and formation of complex compound which has lilac color, changed to yellow-brown a few moments after in the result of oxidation $Co^{2+} \rightarrow Co^{3+}$.

3. Alkalis *(NaOH, KOH)*. Sodium hydroxide forms blue amorphous precipitation of basic salt with Co^{2+} ions:

$$Co^{2+} + OH^- + Cl^- = CoOHCl\downarrow;$$

For example,

$$CoCl_2 + NaOH = CoOHCl\downarrow + NaCl;$$

Excess of alkali converts CoOHCl at heating in $Co(OH)_2$ of pink color:

$$CoOHCl\downarrow + OH^- = Co(OH)_2\downarrow + Cl^-;$$
$$CoOHCl\downarrow + NaOH^- = Co(OH)_2\downarrow + NaCl.$$

Oxiding by air oxygen, $Co(OH)_2$ converts to $Co(OH)_3$ of dark-brown color:

$$4Co(OH)_2 + O_2 + 2H_2O = 4Co(OH)_3$$
$$\begin{array}{l|l} Co^{2+} - 1\overset{-}{e} \rightarrow Co^{3+} & 4 \\ O_2^0 + 4\overset{-}{e} \rightarrow 2O^{2-} & 1 \end{array}$$

If add alkali and hydrogen peroxide H_2O_2 simultaneously to cobalt (II) salt solution, $Co(OH)_3$ forms at once:

$$2CoCl_2 + 4NaOH + H_2O_2 = Co(OH)_3\downarrow + 4NaCl;$$
$$\begin{array}{l|l} Co^{2+} - 1\overset{-}{e} \rightarrow Co^{3+} & 4 \\ 2O^{1-} + 2\overset{-}{e} \rightarrow O_2^0 & 1 \end{array}$$

Test carrying out

Add 1 drop of NaOH to 3-4 drops of Cobalt (II) salt solution. Note color of sediment. Add excess of alkali. Observe change of color of sediment.

4. Ammonium or Potassium Thiocyanide *(NH_4SCN or KSCN)* - crystalline or solution in organic solvents (foe example, acetone) forms the solution of dark blue color:

$$Co^{2+} + 4SCN^- = [Co(SCN)_4]^{2-}.$$

For example,

$$CoCl_2 + 4NH_4SCN = (NH_4)_2[Co(SCN)_4] + 2NH_4Cl.$$

Reaction is very sensitive. Complex compound solves better in the layer of organic solvent, that in water solution.

Test carrying out

Add 4-5 drops of saturated solution of ammonium or potassium thiocyanide in organic solvent to 3-4 drops of Cobalt (II) salt. Shake up content of tube and wait a few seconds. The upper layer is colored in dark-blue color.

Presence of Fe^{3+}-ions in analyzing mixture prevents to determination of cobalt(II), because complex ion $[Fe(SCN)_6]^{3-}$ is more stable that

$Co(SCN)_4]^{2-}$. In such case it is necessary to mask Fe^{3+}-ion added solid NaF, where F^- ions form with Iron (III) ions stable colorless complex ion $[FeF_6]^{3-}$, when cobalt (II) ions don’t compexing with this masking agent. As masking agent orthophosphoric acid and wine acid $H_2C_4H_4O_6$ might be used.

5. Potassium Nitrite KNO_2 in presence of acetic acid oxidizes Co^{2+} to Co^{3+} forming with excess of KNO_2 sediment $K_3[Co(NO_2)_6]$.

In general this reaction is presented as:

$$CoCl_2+7KNO_2+2CH_3COOH=K_3[Co(NO_2)_6]\downarrow+2KCl+2CH_3COOK+$$
$$+\ NO+H_2O.$$

$$\begin{array}{l|l} Co^{2+} - 1\bar{e} \rightarrow Co^{3+} & 1 \\ N^{3+} + 1\bar{e} \rightarrow N^{2+} & 1 \end{array}$$

Test carrying out

To 5-7 drops of cobalt(II) salt solution add crystalline KNO_2 to saturation. Ad to this mixture concentrated acetic acid by drops up to formation of yellow-orange precipitation $K_3[Co(NO_2)_6]$.

6. α-nitrozo-β-naftol $C_{10}H_6(NO)OH$ (Il’inski’s reactant). At the action into ion Co^{2+} this reactant oxidizes Co^{2+} to Co^{3+}, leaved reddish voluminous sediment of intra-complex salt $Co[C_{10}H_6(NO)O]_3$ simultaneously. Reaction is realized in neutral or weak acidic medium.

Test carrying out

Add 1-2 drops of diluted acetic acid and 2-3 drops of fresh-prepared solution of Il’inski’s reactant to 3-4 drops of Cobalt(II) salt solution. Heat mixture in water bath. If necessary, to rub side of tube by glass stick.

Presence of Fe^{3+} ions in analyzing mixture prevents to determination of cobalt(II), because iron(II) ions form brown-reddish sediment with this reactant too.

3.4.4. Characteristic reactions of Nickel cations Ni^{2+}

1. Group reagent *$(NH_4)_2HPO_4$* forms light-green crystalline precipitation with nickel ions:

$$3Ni^{2+} + 2HPO_4^{2-} + 2NH_4OH = Ni_3(PO_4)_2\downarrow + 2NH_4^+ + 2H_2O$$

$$3NiSO_4+2(NH_4)_2HPO_4+2NH_4OH =Ni_3(PO_4)_2\downarrow+3(NH_4)_2SO_4 + 2H_2O.$$

Test carrying out

Add to test-tube 10-12 drops of $(NH_4)_2HPO_4$, 4-6 drops of NH_4OH, 10-12 drops NH_4Cl and 10-12 drops of nickel salt.

Nickel phosphate is diluted in acetic, mineral acids and excess of ammonia:

$$Ni_3(PO_4)_2\downarrow + 6HCl = 3NiCl_2 + 2H_3PO_4;$$

$$Ni_3(PO_4)_2\downarrow + 6CH_3COOH = 3Ni(CH_3COO)_2 + 2H_3PO_4;$$

$$Ni_3(PO_4)_2\downarrow + 18NH_4OH \text{ (excess)} = [Ni(NH_3)_6]_3(PO_4)_2 + 18H_2O.$$

2. Alkalis *(NaOH, KOH).* Sodium hydroxide forms green amorphous precipitation of $Ni(OH)_2$:

$$Ni^{2+} + 2OH^- = Ni(OH)_2\downarrow;$$

For example,

$$NiSO_4 + 2NaOH = Ni(OH)_2\downarrow + Na_2SO_4.$$

Nickel (II) hydroxide dissolves in mineral acids, excess of ammonia, solutions of ammonia salts, but doesn’t soluble in alkali excess.

For example:

$$Ni(OH)_2\downarrow + 6NH_4OH = [Ni(NH_3)_6](OH)_2 + 6H_2O.$$

In presence of chloric or bromic waters in alkaline medium $Ni(OH)_2$ is oxidized to $Ni(OH)_3$ of black-brown color:

$$2Ni(OH)_2\downarrow + Cl_2 + 2NaOH = 2\ Ni(OH)_3\downarrow + 2NaCl.$$

$$\begin{array}{l|l} Ni^{2+} - 1\bar{e} \rightarrow Ni^{3+} & 2 \\ Cl_2^0 + 2\bar{e} \rightarrow 2Cl^- & 1 \end{array}$$

Test carrying out

Add 20-25 drops of NaOH to 8-9 drops of Nickel (II) salt, heat mixture. Observe color of precipitation. Divide precipitation into 5 tubes. Study solubility of $Ni(OH)_2$ in HCl, NH_4Cl, NaOH excess, NH_4OH. Add 3-4 drops of fresh-prepared chloric or bromic water to precipitation in the fifth tube. Observe change of precipitation color.

3. Water ammonia *NH_4OH.* The reaction is carried out in two stages:

the 1st: $2Ni^{2+} + 2SO_4^{2-} + 2NH_4OH = \underset{\text{light-green}}{(NiOH)_2SO_4\downarrow} + 2NH_4^+;$

the 2d: $(NiOH)_2SO_4\downarrow + (NH_4)_2SO_4 + 10NH_4OH = \underset{\text{light-blue solution}}{2[Ni(NH_3)_6]SO_4} + 12H_2O;$

Ni^{2+} doesn’t precipitate by NH_4OH in presence of ammonia salts.

Test carrying out

Add by drops NH_4OH solution to 3-4 drops of nickel salt solution up to basic salt formation (precipitation) and then the excess of NH_4OH up to the dilution of precipitation and formation of complex compound which has light-blue color. Ions of Cu^{2+} and Co^{2+} prevent to this reaction of Ni^{2+}.

4. Dimethylglioxime (Chugaev's reagent) ***$C_4H_8N_2O_2$*** in ammonia medium (pH=9) forms bright pink precipitation of intra-complex salt with Ni^{2+} ions $[Ni(C_4H_7N_2O_2)_2]\downarrow$. Precipitation solves in acids, alkalis, but doesn't dissolve in diluted ammonia solution.

Reaction is very sensitive, concentration limit *c*=1:300000:

$$Ni^{2+} + 2C_4H_8N_2O_2 + 2NH_3 = [Ni(C_4H_7N_2O_2)_2]\downarrow + 2NH_4^+.$$

For example:

$$NiSO_4 + 2C_4H_8N_2O_2 + 2NH_3 = [Ni(C_4H_7N_2O_2)_2]\downarrow + (NH_4)_2SO_4.$$

Test carrying out

Add 12-16 drops of ammonia solution and 8-10 alcohol solution of Chugaev's reagent to 4-5 drops of nickel salt solution. Study solubility of prepared precipitation in mineral acids, alkalis and ammonia solution. For this to divide prepared precipitation into 4 tubes and add corresponding reactant in every doze of precipitation.

Ions of Fe^{2+}, Fe^{3+}, Cu^{2+} prevent to determination of nickel (II) ions with Chugaev's reagent.

3.5. The second group of cations

Group reagent of the second group is $(NH_4)_2HPO_4$.

1. Group reagent ***$(NH_4)_2HPO_4$.*** The reaction is carried out in presence of mixture (NH_4OH + NH_4Cl) which is the buffer mixture, which keeps pH of solution equal to 9. At pH equal to 9 the cation Ca^{2+}, Ba^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+} are deposited as orthophosphates:

$Ca_3(PO_4)_2\downarrow$	$Sr_3(PO_4)_2\downarrow$	$Fe_3(PO_4)_2\downarrow$	$FePO_4\downarrow$	$AlPO_4\downarrow$
white	white	white	yellowish	white

and cation Mg^{2+}, Mn^{2+} are deposited as double salts of Magnesium ammonium phosphate and Manganese ammonium phosphate:

$MgNH_4PO_4\downarrow$,	$MnNH_4PO_4\downarrow$
white	white

For example,

$$3CaCl_2 + 2(NH_4)_2HPO_4 + 2NH_4OH = Ca_3(PO_4)_2\downarrow + 6NH_4Cl + 2H_2O;$$
$$3Ca^{2+} + 2HPO_4^{2-} + 2NH_4OH = Ca_3(PO_4)_2\downarrow + 2NH_4^+ + 2H_2O;$$
$$MnCl_2 + (NH_4)_2HPO_4 + NH_4OH = MnNH_4PO_4\downarrow + 2NH_4Cl + H_2O;$$
$$Mn^{2+} + HPO_4^{2-} + NH_4OH = MnNH_4PO_4\downarrow + H_2O.$$

In contrast to phosphates of the third group, all above mentioned precipitates are not dissolved in excess of NH_4OH. As related to solubility of phosphates in acetic acid, cations of the second group subdivide into two groups:

II-A sub-group - includes cations Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}, Fe^{2+}, phosphates are soluble in acetic acid.

For example,

$$Ca_3(PO_4)_2\downarrow + 4CH_3COOH = 2Ca(CH_3COO)_2 + Ca(H_2PO_4)_2;$$

$$Ca_3(PO_4)_2\downarrow + 4CH_3COOH = 2Ca^{2+} + 4CH_3COO^- + Ca^{2+} + 2H_2PO_4^-.$$

I-B sub-group - includes cations Fe^{3+}, Al^{3+} – phosphates of these cations are insoluble in acetic acid.

Phosphates of both sub-groups are soluble in mineral acids. For example,

$$FePO_4\downarrow + 3H^+ = Fe^{3+} + H_3PO_4;$$

$$FePO_4\downarrow + 3HCl = FeCl_3 + H_3PO_4.$$

Aluminum phosphate due to amphoterity is soluble in alkalis:

$$AlPO_4\downarrow + 4OH^- = AlO_2^- + PO_4^{3-} + 2H_2O;$$

$$AlPO_4\downarrow + 4NaOH = NaAlO_2 + Na_3PO_4 + 2H_2O.$$

Test carrying out

Add 3-5 drops of NH_4OH and 6-8 drops of NH_4Cl to 6-8 drops of $(NH_4)_2HPO_4$ into test-tube and then add 6-8 drops of Calcium salt solution. Make the same action with all the rest cations of second group.

Phosphates of II-A sub-group are soluble in acetic acid and the phosphates of II-B sub-group are soluble in acetic acid.

3.5.1. Characteristic reactions of Magnesium cations Mg^{2+}

1. Group reagent *$(NH_4)_2HPO_4$*. Hydroammonium phosphate at pH equal to 9 (mixture of $NH_4OH + NH_4Cl$) deposits Magnesium ions as white crystalline precipitation of $MgNH_4PO_4$. That is the qualitative reaction of Mg ions is the reaction that is similar to the action of group reagent. The conditions of reaction carrying out are the same described above.

3.5.2. Characteristic reactions of Calcium cations Ca^{2+}

1. Sulfate acid *H_2SO_4* and soluble sulfates. Sulfate acid in presence of acetone forms white precipitation of $CaSO_4$:

$$Ca^{2+} + SO_4^{2-} = CaSO_4\downarrow.$$

For example,

$$CaCl_2 + Na_2SO_4 = CaSO_4\downarrow + 2NaCl.$$

Precipitation $CaSO_4$ is soluble in concentrated solution of Ammonium sulfate $(NH_4)_2SO_4$ as a result of forming of complex salt $(NH_4)_2[Ca(SO_4)_2]$:

$$CaSO_4 + (NH_4)_2SO_4 = (NH_4)_2[Ca(SO_4)_2].$$

Test carrying out

Add 2-3 drops of Sodium sulfate Na_2SO_4 to 4-5 drops of Calcium salt solution.

2. Ammonium oxalate *$(NH_4)_2C_2O_4$*. Ammonium oxalate forms white crystalline precipitation with Calcium ions:

$$Ca^{2+} + C_2O_4^{2-} = CaC_2O_4\downarrow$$

For example,

$$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4\downarrow + 2NH_4Cl.$$

The precipitation is soluble in mineral acids but is insoluble in acetic acid:

$$CaC_2O_4\downarrow + 2H^+ = Ca^{2+} + H_2C_2O_4;$$

$$CaC_2O_4\downarrow + 2HCl = CaCl_2 + H_2C_2O_4.$$

Test carrying out

Add 2-3 drops of Ammonium oxalate to 3-4 drops of Calcium salt solution.

3.5.3. Characteristic reactions of Strontium cations Sr^{2+}

1. Sulfate acid *H_2SO_4* and soluble sulfates. Sulfate acid and soluble sulfates form white precipitation of $SrSO_4$:

$$Sr^{2+} + SO_4^{2-} = SrSO_4\downarrow.$$

For example,

$$Sr(NO_3)_2 + Na_2SO_4 = SrSO_4\downarrow + 2NaNO_3.$$

The precipitation is not soluble in acids.

Test carrying out

Add 2-3 drops of Sodium sulfate Na_2SO_4 solution to 3-4 drops of Strontium salt solution.

2. Ammonium oxalate *$(NH_4)_2C_2O_4$*. Ammonium oxalate forms white crystalline precipitation with Strontium ions:

$$Sr^{2+} + C_2O_4^{2-} = SrC_2O_4\downarrow$$

For example,

$$Sr(NO_3)_2 + (NH_4)_2C_2O_4 = SrC_2O_4 + 2NH_4NO_3.$$

The precipitation is soluble in mineral acids but is insoluble in cold acetic acid:

$$SrC_2O_4^{2-} + 2H^+ = H_2C_2O_4 + Sr^{2+};$$

$$SrC_2O_4 + 2HCl = SrCl_2 + H_2C_2O_4.$$

Test carrying out

Add 2-3 drops of ammonium oxalate solution to 3-4 of Strontium salt solution.

3. Gypsum Water (saturated water solution of $CaSO_4$) forms with ions of Sr^{2+} sediment (in form of white turbidity) $SrSO_4$**.** Gypsum $CaSO_4$ is a slightly soluble substance (SP-$6,1\cdot10^{-5}$), but more soluble, that $SrSO_4$ (SP-$2,8\cdot10^{-7}$). Therefore concentration of SO_4^{2-} in $CaSO_4$ saturated solution is sufficient for exceeding of $SrSO_4$ - Solubility product (SP).

$$Sr^{2+} + SO_4^{2-} = SrSO_4\downarrow.$$

For example,

$$Sr(NO_3)_2 + CaSO_4 = SrSO_4\downarrow + 2Ca(NO_3)_2.$$

Test carrying out

Add 2-3 drops of Gypsum water to 2-3 drops of Strontium salt solution and heat mixture. Observe white turbidity.

3.5.4. Characteristic reactions of Manganese cations Mn^{2+}

Ion Mn^{2+} in acidic medium is oxidized easily to ion MnO_4^- by strong oxidizing agents such as $NaBiO_3$, PbO_2, $(NH_4)_2S_2O_8$ etc. Process is accompanied by change of color of solution. Colorless solutions of Mn^{2+} salts oxidizing to MnO_4^- become crimson-violet.

1. Sodium Bismuthate *$NaBiO_3$*. Sodium bismuthate oxidizes Mn^{2+} to MnO_4^- in presence of nitrate acid:

$$2Mn^{2+} + 5BiO_3^- + 14H^+ = 2MnO_4^- + 5Bi^{3+} + 7H_2O;$$

$$2Mn(NO_3)_2 + 5NaBiO_3 + 16HNO_3 = 2HMnO_4 + 5Bi(NO_3)_3 + 5NaNO_3 + \\ + 7H_2O.$$

$$\begin{array}{l|l} Mn^{2+} - 5e \rightarrow Mn^{7+} & 2 \\ Bi^{5+} + 2e \rightarrow Bi^{3+} & 5 \end{array}$$

Test carrying out

Add small amount of solid Sodium Bismuthate (volume as one match-head) and 15-20 drops of diluted Nitrate acid to only one drop of Manganese salt solution.

2. Hydrogen peroxide *H_2O_2* oxidizes Mn^{2+} up to Mn^{4+} in alkali medium. The black precipitation is formed:

$$Mn^{2+} + H_2O_2 + 2OH^- = H_2MnO_3\downarrow + H_2O;$$

$$Mn(NO_3)_2 + H_2O_2 + 2NH_4OH = H_2MnO_3\downarrow + 2NH_4NO_3 + H_2O.$$

$$\begin{array}{l|l} Mn^{2+} - 2e \rightarrow Mn^{4+} & 1 \\ 2O^{1-} + 2e \rightarrow 2O^{2-} & 1 \end{array}$$

Test carrying out

Add 2-3 drops of 2 N Ammonium hydroxide and 3-4 drops of 3% solution of Hydrogen Peroxide to 2-3 drops of Mn^{2+} salt solution and heat mixture on water bath.

3.5.5. Characteristic reactions of Ferrous cations Fe^{2+}

1. Alkalis *(NaOH, KOH).* Alkali deposits Ferrous ions as precipitation of grey-green color:

$$Fe^{2+} + 2OH^- = Fe(OH)_2\downarrow$$

For example,

$$FeSO_4 + 2NaOH = Fe(OH)_2\downarrow + Na_2SO_4.$$

But color of this precipitation was changed quickly to color of rust as the result of oxidation of Fe^{2+} to Fe^{3+} by air oxygen:

$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3\downarrow$$

$$\begin{array}{l|l} Fe^{2+} - 1e \rightarrow Fe^{3+} & 4 \\ O_2 + 4e \rightarrow 2O^{2-} & 1 \end{array}$$

Add 3-4 drops of sodium hydroxide to 2-3 drops of Ferrous ion salt solution.

2. Potassium ferrocyanide *$K_3[Fe(CN)_6]$* (red blood salt). Potassium ferrocyanide forms precipitation $Fe_3[Fe(CN)_6]_2$ of dark blue color, which is called *Turnbull's blue* with Fe^{2+} ions in acid medium. This reagent is selective for Fe^{2+}:

$$3Fe^{2+} + 2[Fe(CN)_6]^{3-} = Fe_3[Fe(CN)_6]_2\downarrow;$$

For example,

$$3FeSO_4 + 2K_3[Fe(CN)_6] = Fe_3[Fe(CN)_6]_2\downarrow + 3K_2SO_4.$$

The precipitation is not soluble in acids but is decomposed in alkalis with formation of precipitation of $Fe(OH)_2$:

$$Fe_3[Fe(CN)_6]_2 + 6OH^- = 3Fe(OH)_2 + 2[Fe(CN)_6]^{3-};$$

$$Fe_3[Fe(CN)_6]_2 + 6NaOH = 3Fe(OH)_2 + 2Na_3[Fe(CN)_6].$$

Test carrying out

Add 1 drop of HCl and 2-3 drops of Potassium ferrocyanide to 2-3 drops of iron (II) salt solution.

3.5.6. Characteristic reactions of Ferric cations Fe^{3+}

1. Alkalis *(NaOH, KOH).* Alkali deposits ferric ions as precipitation of brown color:

$$Fe^{3+} + 3OH^- = Fe(OH)_3\downarrow$$

For example,

$$FeCl_3 + 3NaOH = Fe(OH)_3\downarrow + 3NaCl.$$

Test carrying out

Add 3-4 drops of sodium hydroxide to 2-3 drops of ferric ion salt solution.

2. Potassium ferricyanide ***K_4 [Fe(CN)$_6$]*** (yellow blood salt)- forms precipitation of dark blue color which is called *Prussian blue* with Fe^{3+} ions in acid medium. Reaction is highly specific and very sensitive (minimum concentration c= 1:1000000):

$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} = Fe_4[Fe(CN)_6]_3\downarrow.$$

For example,

$$4FeCl_3 + 3K_4[Fe(CN)_6] = Fe_4[Fe(CN)_6]_3\downarrow + 12\ KCl.$$

The precipitation is not soluble in acids but is decomposed in alkalis:

$$Fe_4[Fe(CN)_6]_3 + 12OH^- = 4Fe(OH)_3 + 3[Fe(CN)_6]^{4-};$$

$$Fe_4[Fe(CN)_6]_3 + 12NaOH = 4Fe(OH)_3 + 3Na_4[Fe(CN)_6].$$

Test carrying out

Add 1 drop of HCl and 2-3 drops of potassium ferricyanide to 2-3 drops of iron (III) salt solution.

3. Ammonium or Potassium Thiocyanide ***(NH_4SCN or KSCN)*** forms the solution of blood red color:

$$Fe^{3+} + 6SCN^- = [Fe(SCN)_6]^{3-}.$$

For example,

$$FeCl_3 + 6NH_4SCN = (NH_4)_3[Fe(SCN)_6] + 3NH_4Cl.$$

Reaction is very sensitive, especially in presence of organic solvents.

Test carrying out

Add 1 drop of hydrochloric acid solution and 2-3 drops of ammonium Thiocyanide to 2-3 drops of ferric ions.

3.5.7. Characteristic reactions of Aluminium cations Al^{3+}

1. Alkalis ***(NaOH, KOH).*** Sodium or Potassium hydroxide forms white amorphous precipitation with Al^{3+} ions - $Al(OH)_3$ which is the amphoteric hydroxide soluble in acid and alkalis:

$$Al^{3+} + 3OH^- = Al(OH)_3\downarrow.$$

For example,

$$AlCl_3 + 3NaOH = Al(OH)_3\downarrow + 3NaCl,$$

In excess of alkali $Al(OH)_3$ is solved with forming of aluminates:

$$Al(OH)_3 + OH^- = AlO_2^- + H_2O;$$

$$Al(OH)_3\downarrow + NaOH = NaAlO_2 + H_2O.$$

Test carrying out

Add solution of Aluminium salt (by drops) to 1-2 drops of alkali as long as white translucent precipitation is formed.

2. Ammonium chloride ***NH_4Cl.*** Aluminates as salts of weak acids are hydrolyzed in water solutions:

$$AlO_2^- + 2H_2O \leftrightarrow Al(OH)_3\downarrow + OH^-;$$
$$NaAlO_2 + 2H_2O \leftrightarrow Al(OH)_3\downarrow + NaOH.$$

Equilibrium shifts to the left or to the right depends on concentrations of ions H^+ and OH^- in solution, i.e. pH of solution. If solid Ammonium Chloride or saturated solution of this salt add to alkaline solution of Aluminate, NH_4Cl reacts with NaOH:

$$NH_4Cl + NaOH = NaCl + NH_4OH.$$

But formation of NH_4OH leads to reducing of pH up to 7-8 and equilibrium shifts to the direction of Aluminium Hydroxide precipitating. The best results are observed in mixture at heating. In general, reaction of $NaAlO_2$ in presence of NH_4Cl is the next view:

$$AlO_2^-+NH_4^++2H_2O=Al(OH)_3\downarrow+NH_4OH;$$
$$NaAlO_2 + NH_4Cl + 2H_2O = Al(OH)_3\downarrow + NH_4OH + NaCl.$$

Test carrying out

Add 1-2 drops of 2 N NaOH to 3-4 drops of Al^{3+} solution up to $Al(OH)_3$ precipitation formation and then add the excess of the same alkali up to precipitation dilution. Add 2-3 mL of DW and NH_4Cl (crystals) to the received Aluminate up to saturated solution formation. Heat mixture on water bath.

3.6. The fourth group of cations

It is studied two representatives of this group – ions of Ag^+ and Pb^{2+}, formed slightly soluble precipitations of Chlorides, don’t soluble in diluted acids. Solubility of AgCl and $PbCl_2$ in water, excess of HCl, ammonia solution is of great importance for separation of these cations.

Group reagent – ***diluted HCl***. HCl (and soluble chlorides) deposits Ag^+ and Pb^{2+} in form of white precipitations of AgCl and $PbCl_2$, not soluble in diluted HNO_3 and H_2SO_4:

$$Ag^+ + Cl^- = AgCl\downarrow;$$
$$Pb^{2+} +2Cl^- = PbCl_2\downarrow.$$

For example,

$$AgNO_3 +HCl = AgCl\downarrow + HNO_3;$$
$$Pb(NO_3)_2 + 2HCl = PbCl_2\downarrow + 2HNO_3.$$

Test carrying out

Add the same quantity of diluted HCl 2-3 drops of Silver salt solution or Lead salt solution. Formed white precipitations of AgCl and $PbCl_2$ divide into 4 tubes and study their solubility in hot H_2O, concentrated water ammonia, $(NH_4)_2CO_3$, concentrated HCl.

AgCl dissolves in:

- concentrated water ammonia:

$$AgCl\downarrow + 2NH_4OH = [Ag(NH_3)_2]^+ + Cl^- + 2H_2O \text{ or}$$

$$AgCl\downarrow + 2NH_4OH = [Ag(NH_3)_2]Cl + 2H_2O;$$

- excess of $(NH_4)_2CO_3$:

$$AgCl\downarrow + 2NH_4^+ + CO_3^{2-} = [Ag(NH_3)_2]^+ + Cl^- + 2H_2O + CO_2\uparrow \text{ or}$$

$$AgCl\downarrow + (NH_4)_2CO_3 = [Ag(NH_3)_2]Cl + 2H_2O + CO_2\uparrow.$$

- concentrated HCl or saturated solution of NaCl:

$$AgCl\downarrow + 2H^+ + 2Cl^- = 2H^+ + [AgCl_3]^- \text{ or}$$

$$AgCl\downarrow + 2HCl = H_2[AgCl_3].$$

Sediment $PbCl_2$ in contrast to AgCl dissolves well in hot DW (near 10 g/L). This moment is used for separate off AgCl and $PbCl_2$.

$PbCl_2$ dissolves in:

- concentrated HCl or saturated solution of NaCl:

$$PbCl_2\downarrow + 2H^+ + 2Cl^- = 2H^+ + [PbCl_4]^{2-} \text{ or}$$

$$PbCl_2\downarrow + 2HCl = H_2[PbCl_4].$$

If this solution dilutes of water, $PbCl_2$ will precipitate again.

3.6.1. Characteristic reactions of Silver cations Ag^+

1. Water ammonia *NH_4OH*, reacting with Ag^+, precipitates silver in form of Ag_2O, which dissolves in excess of reactant:

$$Ag^+ + NH_4OH = AgOH\downarrow + NH_4^+;$$

$$2AgOH\downarrow = Ag_2O\downarrow + H_2O;$$

$$Ag_2O\downarrow + 4\ NH_4OH = 2[Ag(NH_3)_2]^+ + 2OH^- + 3H_2O \text{ or}$$

$$AgNO_3 + NH_4OH = AgOH\downarrow + NH_4NO_3;$$

$$Ag_2O\downarrow + 4\ NH_4OH = 2[Ag(NH_3)_2]OH + 3H_2O.$$

Test carrying out

Add by drops ammonia solution to 1-2 drops of silver nitrate solution till precipitation formation. Observe dissolving of turbidity at adding of excess of ammonia.

3.6.2. Characteristic reactions of Lead cations Pb^{2+}

1. Potassium Iodide *KI* isolates yellow sediment of PbI_2 from Lead (II) solutions. PbI_2 dissolves in boiling water. After cooling PbI_2 is precipitated again in form of goldish-yellow crystals (sometimes this reaction is called reaction of “gold rain”). This reaction is used for identification of Pb^{2+} in mixtures and substances.

Condition of this reaction realization: pH less than 7 (add a few drops of diluted acetic acid), fast cooling.

$$Pb^{2+} + 2I^- = PbI_2\downarrow.$$

For example,

$$Pb(NO_3)_2 + 2KI = PbI_2\downarrow + 2\ KNO_3.$$

Test carrying out

Add 1-3 drops of potassium iodide solution of 2 drops of lead nitrate or lead acetate solution acidified by 1 drop of acetic diluted acid. Add DW to formed yellow sediment (5-7 mL) and boil mixture in water bath. After complete dissolving of precipitation cool quickly tube at stream of cool running water. For acceleration of re-crystallization rub tube sides by glass stick.

2. Potassium Chromate (Dichromate) *K_2CrO_4 ($K_2Cr_2O_7$)* forms yellow precipitation $PbCrO_4$ with ions Pb^{2+}. This sediment doesn't dissolve in acetic and hydrochloric acids, but solutes in alkalis and nitrate acid. Conditions: pH less then 7 (in presence of acetic acid), absence of reducing agents, reduced Cr^{6+} till Cr^{3+} (for example, Fe^{2+}), absence of cations, formed with CrO_4^{2-} sediments:

$$Pb^{2+} + CrO_4^{2-} = PbCrO_4\downarrow;$$

$$\text{or } 2Pb^{2+} + Cr_2O_7^{2-} + H_2O = 2PbCrO_4\downarrow + 2H^+.$$

For example:

$$Pb(NO_3)_2 + K_2CrO_4 = PbCrO_4\downarrow + 2KNO_3; \text{ or}$$

$$2Pb(CH_3COO)_2 + K_2Cr_2O_7 + H_2O = 2PbCrO_4\downarrow + 2KCH_3COO + 2CH_3COOH.$$

Test carrying out

Add 1-2 drops of potassium chromate or dichromate solution to 1-2 drops of lead salt solution. Yellow precipitate formed.

Note, that presence of reducing agents (Fe^{2+}, Mn^{2+}) prevents reaction owing to reduction of Cr^{6+} till Cr^{3+}. In presence of Ag^+ brick-red sediment Ag_2CrO_4 or dark-red $Ag_2Cr_2O_7$ is precipitated.

3. Diluted Sulfate Acid *H_2SO_4* and soluble sulfates precipitate Pb^{2+} cation in the form of white crystalline precipitation $PbSO_4$. this sediment is dissolved in excess of diluted sulphate acid, but is dissolved in alkalis, ammonia acetate and ammonia salt of wine acid (tartrate), concentrated H_2SO_4 and HCl. Conditions of reactions: pH less than 7, because lead sulphate is dissolved in alkalis, absence of ammonia salts of acetic or wine acids, absence of Ca^{2+} and Sr^{2+} ions in examined solution:

$$Pb^{2+} + SO_4^{2-} = PbSO_4.$$

For example:

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4\downarrow + 2HNO_3.$$

Test carrying out

Add 1-2 drops of diluted sulphate acid to 2-3 drops of lead salt solution. Observe formation of the white crystalline precipitation. Content of tube divide into two tubes and examine its solubility in excess of H_2SO_4 (diluted) and excess of alkali NaOH.

3.7. Qualitative analysis of anions

Universally recognized anion classification doesn't exist.

Anion division into groups is based on solubility of their Barium and Silver salts (Table 7).

Table 7. Classification of anions

Group	I	II	III
Anions	SO_4^{2-}; SO_3^{2}; CO_3^{2-}; PO_4^{3-}; SiO_3^{2-}; BO_2^- (or $B_4O_7^{2-}$); MoO_4^{2-}	Cl^-, Br^-, I^-	NO_3^-, NO_2^-, CH_3COO^-
Group reagent	$BaCl_2$ in neutral or weakly alkaline medium	$AgNO_3$ in presence of diluted HNO_3	There is no group reagent in the third group
Properties of precipitates	Barium salts are insoluble in H_2O but are soluble in diluted acids (exclusion is $BaSO_4$)	Silver salts insoluble in H_2O and HNO_3	Barium and silver salts are soluble in H_2O

3.8. The first group of anions

1. *$BaCl_2$* as the group reagent deposits the first group anions in the form of white precipitates: $BaSO_4$, $BaSO_3$, $BaCO_3$, $Ba_3(PO_4)_2$, $Ba(BO_2)_2$ or BaB_2O_7, $BaSiO_3$, $BaMoO_4$. All precipitates are soluble in Hydrochloric HCl and Nitrate acids HNO_3, excluding $BaSO_4$. Precipitates $Ba_3(PO_4)_2$, $BaCO_3$ and $Ba(BO_2)_2$ solve in Acetic Acid.

$$SO_4^{2-} + Ba^{2+} = BaSO_4\downarrow;$$
$$SO_3^{2-} + Ba^{2+} = BaSO_3\downarrow;$$
$$2PO_4^{3-} + 3Ba^{2+} = Ba_3(PO_4)_2\downarrow;$$
$$B_4O_7^{2-} + 2Ba^{2+} + H_2O = 2Ba(BO_2)_2\downarrow + 2H^+;$$
$$CO_3^{2-} + Ba^{2+} = BaCO_3\downarrow;$$
$$SiO_3^{2-} + Ba^{2+} = BaSiO_3\downarrow;$$
$$MoO_4^{2-} + Ba^{2+} = BaMoO_4\downarrow.$$

For example,

$$Na_2SO_4 + BaCl_2 = BaSO_4\downarrow + 2NaCl;$$
$$Na_2SO_3 + BaCl_2 = BaSO_3\downarrow + 2NaCl;$$

$$2Na_3PO_4 + 3BaCl_2 = Ba_3(PO_4)_2\downarrow + 6NaCl;$$
$$Na_2B_4O_7 + 2BaCl_2 + H_2O = 2Ba(BO_2)_2\downarrow + 2NaCl + 2HCl;$$
$$Na_2CO_3 + BaCl_2 = BaCO_3\downarrow + 2NaCl;$$
$$Na_2SiO_3 + BaCl_2 = BaSiO_3\downarrow + 2NaCl;$$
$$(NH_4)_2MoO_4 + BaCl_2 = BaMoO_4\downarrow + 2NH_4Cl.$$

Test carrying out

pH of analyzed solutions must be equal or more than 7 (neutral or slightly alkaline medium). Add 1-2 drops of $BaCl_2$ solution to 2-3 drops of corresponding salts solutions (Na_2SO_4, Na_2SO_3, Na_3PO_4, $Na_2B_4O_7$, Na_2CO_3, Na_2SiO_3, $(NH_4)_2MoO_4$). Observe formation of white precipitates in all tubes. Note, that $Ba(BO_2)_2$ precipitates only from concentrated solution.

Study solubility of every precipitate in H_2SO_4 (or HCl). Observe gassing during dissolving of $BaCO_3$ and $BaSO_3$.

2. *AgNO₃* or Silver soluble salts forms precipitates with all anions of the first group: Ag_2SO_4, Ag_2SO_3, $AgBO_2$, Ag_2MoO_4, Ag_2CO_3 – white; Ag_2SiO_3, Ag_3PO_4 – yellow. Ag_2SO_4 sediments of concentrates solutions only.

These precipitates are soluble in mineral and organic acids. Ag_2SO_4 is soluble in water visibly in hot water; Ag_2SiO_3 is decomposed with formation of H_2SiO_3 in the form of gelatinized precipitate.

Test carrying out

pH of medium is more than 7.

$$SO_4^{2-} + 2Ag^+ = Ag_2SO_4\downarrow;$$
$$SO_3^{2-} + 2Ag^+ = Ag_2SO_3\downarrow;$$
$$PO_4^{3-} + 3Ag^+ = Ag_3PO_4\downarrow;$$
$$B_4O_7^{2-} + 4Ag^+ + H_2O = 4AgBO_2\downarrow + 2H^+;$$
$$CO_3^{2-} + 2Ag^+ = Ag_2CO_3\downarrow;$$
$$SiO_3^{2-} + 2Ag^+ = Ag_2SiO_3\downarrow;$$
$$MoO_4^{2-} + 2Ag^+ = Ag_2MoO_4\downarrow.$$

For example,

$$Na_2SO_4 + 2AgNO_3 = BaSO_4\downarrow + 2NaNO_3;$$
$$Na_2SO_3 + 2AgNO_3 = BaSO_3\downarrow + 2NaNO_3;$$
$$Na_3PO_4 + 3AgNO_3 = Ag_3PO_4\downarrow + 3NaNO_3;$$
$$Na_2B_4O_7 + 4AgNO_3 + H_2O = 4AgBO_2\downarrow + 2NaNO_3 + 2HNO_3;$$
$$Na_2CO_3 + 2AgNO_3 = Ag_2CO_3\downarrow + 2NaNO_3;$$
$$Na_2SiO_3 + 2AgNO_3 = Ag_2SiO_3\downarrow + 2NaNO_3;$$
$$(NH_4)_2MoO_4 + 2AgNO_3 = Ag_2MoO_4\downarrow + 2NH_4NO_3.$$

Add 1-2 drops of $AgNO_3$ solution to 2-3 drops of corresponding salts solutions (Na_2SO_4, Na_2SO_3, Na_3PO_4, $Na_2B_4O_7$, Na_2CO_3, Na_2SiO_3, $(NH_4)_2MoO_4$). Observe formation of precipitates in all tubes. Study solubility of every precipitate in HNO_3 (or HCl). Observe dissolving of precipitates.

3. Sulfate acid *H_2SO_4* (or *HCl*) decomposes salts of Sulfite acid with gassing of SO_2:

$$SO_3^{2-} + 2H^+ = H_2SO_3;$$

$$H_2SO_3 \rightarrow SO_2\uparrow + H_2O.$$

Isolation of SO_2 is detected by specific odor (similar to odor of in moment of striking a match) or discoloring of permanganate solution.

Interaction of sulfate acid with salts of carbonate acid is accompanied by the gassing of CO_2. Presence of carbonic gas is detected by turbidity of lime or baryta water:

$$CO_3^{2-} + 2H^+ = H_2O + CO_2\uparrow;$$

$$CO_2\uparrow + Ca(OH)_2 \rightarrow CaCO_3\downarrow + H_2O.$$

Interaction of sulfate acid with salts of silicate acid is accompanied by decomposition of the last ones with formation of hydrosol (a colloid with water as the dispersing medium) of silicate acid:

$$SiO_3^{2-} + 2H^+ = H_2SiO_3\downarrow.$$

Salts of molybdate and borate acids are decomposed by strong mineral acids with formation of free slightly soluble acids:

$$MoO_4^{2-} + 2H^+ = H_2MoO_4;$$

$$B_4O_7^{2-} + 2H^+ + 5H_2O = 4H_3BO_3.$$

Anions of multibased acids (for example, PO_4^{3-}), reacting with H_2SO_4, form acidic salts or free acids, for example:

$$PO_4^{3-} + H_2SO_4 = HSO_4^- + HPO_4^{2-};$$

$$HPO_4^{2-} + H_2SO_4 = HSO_4^- + H_2PO_4^-;$$

$$H_2PO_4^- + H_2SO_4 = HSO_4^- + H_3PO_4.$$

Test carrying out

Add 2-3 drops of 2 N solution of H_2SO_4 to 2-3 drops of Carbonate salt or Sulfite salt or Silicate salt (for example, Na_2CO_3, Na_2SO_3 or Na_2SiO_3 correspondently).

4. Oxiding agents (*$KMnO_4$, $K_2Cr_2O_7$* etc.) react with Sulfites, reducting to Sulfates:

$$2KMnO_4 + 5Na_2SO_3 + 8H_2SO_4 = 2MnSO_4 + 5Na_2SO_4 + K_2SO_4 +$$
$$+ 8H_2O.$$

5. Reducing agents (*Mn^{2+}, Fe^{2+}, Sn^{2+}* etc.) react with anions of Sulfite and Molybdate acids:

$$2SnCl_2 + Na_2SO_3 + 6\,HCl = 2SnCl_4 + S + 2NaCl + 3H_2O.$$

$$\begin{array}{l|l} S^{4+} + 4\bar{e} \rightarrow S^0 & 1 \\ Sn^{2+} - 2\bar{e} \rightarrow Sn^{4+} & 2 \end{array}$$

$$2FeSO_4 + 3(NH_4)_2MoO_4 + H_2SO_4 = Fe_2(SO_4)_3 + 2(NH_4)_3MoO_3 + \\ + H_2O.$$

$$\begin{array}{l|l} Mo^{6+} + 3\bar{e} \rightarrow Mo^{3+} & 2 \\ 2Fe^{2+} - 2\bar{e} \rightarrow 2Fe^{3+} & 3 \end{array}$$

3.8.1. Characteristic reactions of Sulfate anions SO_4^{2-}

1. Barium Chloride (group reagent) *$BaCl_2$*. Insolubility of $BaSO_4$ precipitation in HCl indicates the presence of SO_4^{2-} ions (see above 3.8).

2. Soluble Lead salts *($Pb(NO_3)_2$ or $Pb(CH_3COO)_2$)*. The control reaction with this reagent should be performed. Pb^{2+} precipitates anions SO_4^{2-} in the form of white precipitation $PbSO_4$, insoluble in acids but soluble in alkalis (in contrast to $BaSO_4$).

$$SO_4^{2-} + Pb^{2+} = PbSO_4\downarrow;$$

$$PbSO_4\downarrow + 4OH^- = PbO_2^{2-} + SO_4^{2-} + 2H_2O.$$

For example,

$$Na_2SO_4 + Pb(NO_3)_2 = PbSO_4\downarrow + 2NaNO_3;$$

$$PbSO_4\downarrow + 4NaOH\ (\text{excess}) = Na_2PbO_2 + Na_2SO_4 + 2H_2O.$$

Test carrying out

Add 1-2 drops of $Pb(NO_3)_2$ or $Pb(CH_3COO)_2$ to 2-3 drops of Sulfate salt. Divide precipitation between two test-tubes. To the first tube add 3-5 drops of Nitrate acid, to the second one - 3-6 drops of alkali. Observe dissolving of precipitation.

3.8.2. Characteristic reactions of Sulfite anions SO_3^{2-}

1. Barium Chloride (group reagent) *$BaCl_2$*. White precipitate of barium sulfite (see above 3.8).

2. Dilute hydrochloric acid *HCl* (or dilute sulfate acid *H_2SO_4*): decomposition, more rapidly on warming, with the evolution of Sulfur oxide (IV) SO_2:

$$SO_3^{2-} + 2H^+ = H_2SO_3;$$
$$H_2SO_3 \rightarrow SO_2\uparrow + H_2O.$$

Foe example:

$$Na_2SO_3 + 2HCl = SO_2\uparrow + 2NaCl + H_2O.$$

The gas may be identified by its suffocating odor of burning sulfur, or by the green coloration, due to the formation of Chromium (III) ions, produced when a filter paper, moistened with acidified potassium dichromate solution, is held over the mouth of the test-tube:

$$2SO_2 + Cr_2O_7^{2-} + 2H^+ = 2Cr^{3+} + 3SO_4^{2-} + H_2O.$$

Another method of identification of the gas is to hold a filter paper, moistened with Potassium Iodate (V) $KClO_3$ and starch solution, in the vapor, when a blue color, owing to the formation of free iodine, is observable:

$$5SO_2 + 2IO_3^- + 4H_2O = I_2 + 5SO_4^{2-} + 5H^+.$$

Test carrying out

Place 8-10 drops of fresh-prepared solution of Sodium Sulfite Na_2SO_3 upon test-tube, add 8-10 drops of 2N HCl. Identificate the gas using one of the above described methods.

3. Lime water *$Ca(OH)_2$*. This test is carried out by adding dilute hydrochloric acid to the solid sulfite, and bubbling the evolved gas through lime water; a white precipitate of calcium sulfite $CaSO_3$ is formed:

$$SO_3^{2-} + Ca^{2+} = CaSO_3\downarrow.$$

For example:

$$Na_2SO_3 + Ca(OH)_2 = CaSO_3\downarrow + 2NaOH.$$

The precipitate dissolves on prolonged passage of the gas, due to the formation of hydrosulfite ions:

$$CaSO_3\downarrow + SO_2 + H_2O = Ca^{2+} + 2HSO_3^-.$$

A turbidity is also produced by carbonates; Sulfur oxide (IV) must therefore be first removed when testing for the latter. This may be effected by adding potassium dichromate solution to the test-tube before acidifying. The dichromate oxidizes and destroys the Sulfur oxide (IV) without affecting the Carbon oxide (IV). In the case of using of acidified permanganate solution the visual effect is decolorizing.

Test carrying out

This test is best carried out in the apparatus shown in fig. 10.

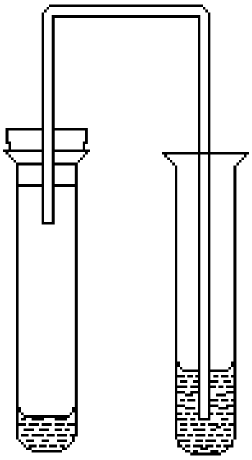


Figure 10 – Apparatus for gas testing

The solid Na_2SO_3 (near 0,05-0,1 g) is placed in to the test-tube or small distilling flask (10-25 mL capacity), dilute hydrochloric acid added, and the cork immediately replaced. The gas which is evolved (warming may be necessary) is passed into lime water contained in the test-tube; the production of a turbidity indicates the presence of a sulfite.

4. Strong oxiding agents (*$KMnO_4$* or solution of free *I_2*). Potassium permanganate solution, acidified with dilute sulfate acid before the testing, reacts with Sulfite solution with discoloration, owing to reduction to Manganese (II) ions:

$$5SO_3^{2-} + 2MnO_4^{-} + 6H^{+} = 2Mn^{2+} + 5SO_4^{2-} + 3H_2O.$$

For example,

$$2KMnO_4 + 5Na_2SO_3 + 8H_2SO_4 = 2MnSO_4 + 5Na_2SO_4 + K_2SO_4 + \\ + 8H_2O.$$

$$\begin{array}{l|l} Mn^{7+} + 5\bar{e} \rightarrow Mn^{2+} & 2 \\ S^{4+} - 2\bar{e} \rightarrow S^{6+} & 5 \end{array}$$

If to use free iodine solution, visual effect of reaction is in discoloration of solution owing to transformation of free I_2 to colorless iodide-ions:

$$2SO_3^{2-} + I_2 = S_2O_6^{2-} + 2I^{-}.$$

For example:

$$2Na_2SO_3 + I_2 = Na_2S_2O_6 + 2NaI.$$

$$\begin{array}{l|l} 2S^{4+} + 4\bar{e} \rightarrow 2S^{5+} & 1 \\ I_2 - 2\bar{e} \rightarrow 2I^{-} & 2 \end{array}$$

Test carrying out

Place 2 drops of Potassium permanganate upon test-tube, acidify by adding of 2-3 drops of diluted sulfate acid and add 5-6 drops of fresh-prepared solution of Sodium Sulfite Na_2SO_3. To observe discoloration of solution.

Repeat the previous test with iodine solution.

3.8.3. Characteristic reactions of Carbonate anions CO_3^{2-}

1. Barium Chloride (group reagent) *$BaCl_2$*. Precipitation solubility of $BaCO_3$ in HCl with gas bubbles of CO_2 isolation indicates the presence of CO_3^{2-} ions in solution (see 3.8, item 1).

Isolated gas (CO_2) has to be put into solution of baryta water $Ba(OH)_2$ or limewater - $Ca(OH)_2$ and to observe the solution turbidity caused by the formation of $BaCO_3$ or $CaCO_3$ precipitations (barium carbonate or calcium carbonate) (see above 3.8.2, fig. 10).

2. Mineral acids *(H_2SO_4, HCl, HNO_3 etc.)*, and acetic acid CH_3COOH decompose carbonates with gassing of CO_2. Presence of CO_2 may be indicated using baryta water $Ba(OH)_2$ or lime water as in previous experiment:

$$CO_3^{2-} + 2H^+ = CO_2\uparrow + H_2O;$$

$$Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O.$$

For example,

$$Na_2CO_3 + 2HCl = CO_2\uparrow + 2NaCl + H_2O;$$

$$\text{or } MgCO_3\downarrow + H_2SO_4 = MgSO_4 + CO_2\uparrow + H_2O.$$

Test carrying out

Add 1-2 mL of 2 N acid (H_2SO_4 or HCl, or CH_3COOH) to 0,5-1,0 mL of Carbonate solution in test-tube (see fig. 10) and the cork immediately replaced. The gas which is evolved (warming may be necessary) is passed into lime water contained in the test-tube; the production of a turbidity indicates the presence of a carbonate.

3.8.4. Characteristic reactions of Phosphate anions PO_4^{3-}

1. Magnesia mixture *($MgCl_2$ in presence of buffer mixture NH_4OH + NH_4Cl).* This reaction is similar to characteristic reaction of Mg^{2+} ions. Magnesia mixture reacts with phosphates forming white crystalline precipitation $MgNH_4HPO_4\downarrow$:

$$HPO_4^{2-} + Mg^{2+} + NH_4OH = MgNH_4PO_4\downarrow + H_2O;$$

For example,

$$Na_2HPO_4 + MgCl_2 + NH_4OH = MgNH_4PO_4\downarrow + 2NaCl + H_2O.$$

Test carrying out

Add to test tube 2–3 drops of $MgCl_2$ and NH_4Cl solutions, add to prepared mixture 2–3 drops of Na_2HPO_4 or $(NH_4)_2HPO_4$ solution. Shuffle mixture and add solution of NH_4OH to alkali reaction of medium.

2. Molybdenum liquid (*the mixture of $(NH_4)_2MoO_4$ and HNO_3*). As the result of reaction the yellow precipitation $(NH_4)_3H_4[P(Mo_2O_7)_6]$ is formed. Precipitation composition can be written as follows:

$$HPO_4^{2-}+3NH_4^{+}+12MoO_4^{2-}+23H^{+} = (NH_4)_3H_4[P(Mo_2O_7)_6]\downarrow+10H_2O;$$

$$Na_2HPO_4+12(NH_4)_2MoO_4+23HNO_3=(NH_4)_3H_4[P(Mo_2O_7)_6]\downarrow+$$
$$+ 2NaNO_3+21NH_4NO_3+10H_2O.$$

Test carrying out

Add 5-8 drops of Molybdenum liquid to 2-3 drops of Phosphate solution. Boil mixture.

3.8.4. Characteristic reactions of Borate anions $B_4O_7^{2-}$ (BO_2^-)

1. Barium Chloride (group reagent) *$BaCl_2$*. White precipitate of barium methaborate $Ba(BO_2)_2$ from concentrated solution of borates (see above 3.8).

2. Silver nitrate *$AgNO_3$* precipitates from moderate concentrated solutions at room temperature white Silver Methaborate:

$$B_4O_7^{2-} + 2Ag^{+} + 3H_2O = 2AgBO_2\downarrow + 2H_3BO_3.$$

For example,

$$Na_2B_4O_7 + 2AgNO_3 + 3H_2O = 2AgBO_2\downarrow + 2H_3BO_3 + 2NaNO_3.$$

It forms brown precipitate of Silver Oxide in very diluted solutions at cool and in more concentrated ones at heating:

$$2AgBO_2 + 3H_2O = Ag_2O\downarrow + 2H_3BO_3.$$

Test carrying out

Add 1-2 drops of Silver Nitrate solution to 10-15 drops of Borax solution (10-15%). Observe slow formation of white precipitate.

3. Flame test. Bringing of volatile Boron compounds (Methyl Ether $(CH_3O)_3$ B or Ethyl Ether $(C_2H_5O)_3B$ or free Borate acid) in colorless flame, it is observed specific light-green coloring of flame:

$$B_4O_7^{2-} + 2H^{+} + 5H_2O = 4H_3BO_3;$$

$$H_3BO_3 + 3C_2H_5OH = B(OC_2H_5)_3 + 3H_2O;$$

$$2B(OC_2H_5)_3 + 18O_2 \xrightarrow{t} B_2O_3 + 12CO_2 +15H_2O.$$

For example,

$$Na_2B_4O_7 + H_2SO_4\ (conc) + 5H_2O = 4H_3BO_3 + Na_2SO_4;$$

$$H_3BO_3 + 3C_2H_5OH = B(OC_2H_5)_3 + 3H_2O;$$

$$2B(OC_2H_5)_3 + 18O_2 \xrightarrow{t} B_2O_3 + 12CO_2 + 15H_2O.$$

Test carrying out

Add 0,5 – 1 mL of examined Borate solution in to small evaporating dish and heat to dry residue. Add near 1 mL concentrated Sulfate acid (**Carefully!**), 1-2 mL of ethyl alcohol and set fire to surface of mixture in the plate. Flame colors in green.

3.8.5. Characteristic reactions of Molybdate anions MoO_4^{2-}

1. Barium Chloride (group reagent) *$BaCl_2$* white precipitate of Barium Molybdate $BaMoO_4$ from concentrated solution of molybdates (see above 3.8).

2. Ammonium or Potassium Thiocyanide *(NH_4SCN or $KSCN$)* forms complex rodanides with molybdates. The most colored red complex is Molybdenum (V) rodanide one. Ions Fe^{3+} prevent to this reaction. Fe^{3+} ions are masked reducing to Fe^{2+} added compounds of Sn^{2+}. The last reagent in the same time reduces Mo^{6+} to Mo^{5+}:

$$2\ MoO_4^{2-} + Sn^{2+} + 10SCN^- + 12H^+ = 2[MoO(SCN)_5]^{2-} + Sn^{4+} + 6H_2O.$$

For example,

$$2Na_2MoO_4 + SnCl_2 + 10NH_4SCN + 12HCl = 2Na_2[MoO(SCN)_5] +$$
$$+ SnCl_4 + 10NH_4Cl + 6H_2O.$$

Test carrying out

Acidify 1 mL of Sodium Molybdate solution by 0,5 mL of diluted Hydrochloric acid, add 1-2 mL of saturated Tin (II) chloride solution and add 5-6 drops of 10% Ammonium Thiocyanide (rodanide). Observe red color of solution.

3. Hydrogen Peroxide *H_2O_2* in presence of concentrated ammonia NH_4OH forms red colored solution of Permolybdate. Color is unstable, may be observe during 10-30 sec after Peroxide was added:

$$MoO_4^{2-} + H_2O_2 \leftrightarrow [MoO_5]^{2-} + H_2O$$

$$\begin{array}{l|l} Mo^{6+} - 2\bar{e} \rightarrow Mo^{8+} & 1 \\ 2O^{1-} + 2\bar{e} \rightarrow 2O^{2-} & 1 \end{array}$$

For example,

$$Na_2MoO_4 + 2NH_4OH \leftrightarrow (NH_4)_2MoO_4 + 2NaOH;$$

$$(NH_4)_2MoO_4 + H_2O_2 = (NH_4)_2[MoO_5] + H_2O.$$

Test carrying out

Add 1 mL of concentrated Ammonia to 1-2 mL of Sodium Molybdate solution in small evaporating dish and heat to dry residue. Add by drops 10% Hydrogen Peroxide H_2O_2. Observe red color of solution at the moment of reaction.

3.8.6. Characteristic reactions of Silicate anions SiO_3^{2-}

It is known a few Silicate acids: Methasilicate H_2SiO_3, Ortho-Silicate H_4SiO_4, poly-silicates $H_2Si_2O_5$, and, in general, $xSiO_2 \cdot yH_2O$. All silicate acids don't solve in water, bur form colloid solutions. Only silicates of alkali metals solve in water. Qualitative reactions of Silicate anions are based on this property to form colloid solutions of silicate acids.

1. Barium Chloride (group reagent) *BaCl₂* - white precipitate of Barium Silicate $BaSiO_3$ from concentrated solution of soluble silicates (see above 3.8).

2. Diluted acids *(HCl, H₂SO₄)* isolate voluminous jellied precipitate of silicate acids from concentrated silicate solutions. At certain conditions (high concentration of silicate, slowly adding of mineral acid by drops) this precipitate coagulates completely and don't pour out from tube. If mineral acid was added quickly to diluted solution of silicate, silicate acids form colloid solution and don't precipitate for a long time.

$$SiO_3^{2-} + 2H^+ = H_2SiO_3\downarrow.$$

For example,

$$Na_2SiO_3 + 2HCl = H_2SiO_3\downarrow + 2NaCl.$$

Test carrying out

Add slowly by drops concentrated mineral acid (for example, HCl) to 5-10 drops of concentrated Sodium Silicate solution in tube. Observe formation of dense jelled milky precipitate.

3. Silver nitrate *AgNO₃* isolates yellow precipitate of Silver Silicate from concentrated silicate solutions:

$$SiO_3^{2-} + 2Ag^+ = Ag_2SiO_3\downarrow + 2NO_3^-.$$

For example,

$$Na_2SiO_3 + 2AgNO_3 = Ag_2SiO_3\downarrow + 2NaNO_3.$$

Test carrying out

Add slowly by drops Silver Nitrate solution to 5-10 drops of concentrated silicate solution in the tube.

4. Ammonium Salts (for example, *NH_4Cl*) isolate jelly precipitate of silicate acids more completely, than mineral acids:

$$SiO_3^{2-} + 2NH_4^+ + 2H_2O = H_2SiO_3\downarrow + 2NH_4OH.$$

For example,

$$Na_2SiO_3 + 2NH_4Cl + 2H_2O = H_2SiO_3\downarrow + 2NH_4OH + 2NaCl.$$

Silicate acids precipitate more quickly at heating.

Test carrying out

Add 3-6 drops of concentrated Ammonia Chloride solution to 5-10 drops of Sodium Silicate solution, heat mixture. Observe formation of jelly milky precipitate.

3.9. The second group of anions

Silver Nitrate *$AgNO_3$* (group reagent) in presence of HNO_3. The group reagent deposits the ions of Cl^-, Br^-, I^- in the form: AgCl - white precipitation; AgBr - primrose one; AgI - light yellow one.

HNO_3 is added to avoid precipitation formation of the first group anions with $AgNO_3$.

3.9.1. Characteristic reactions of Chloride anions Cl^-

1. Silver Nitrate *$AgNO_3$* in presence of HNO_3 reacts with Cl^- with forming of white precipitation AgCl. Formed white precipitation of AgCl is dissolved in NH_4OH with the formation of complex compound - diaminosilver chloride $[Ag(NH_3)_2]Cl$.

$$AgCl + 2NH_4OH = [Ag(NH_3)_2]Cl + 2H_2O;$$

$$AgCl + 2NH_4OH = [Ag(NH_3)_2]^+ + Cl^- + 2H_2O.$$

At subsequent acidification of solution by nitrate acid white precipitation of silver chloride (AgCl) is formed again:

$$Ag(NH_3)_2]Cl + 2HNO_3 = AgCl\downarrow + 2NH_4NO_3;$$

$$[Ag(NH_3)_2]^+ + Cl^- + 2H^+ = AgCl\downarrow + 2NH_4^+$$

Test carrying out

Add 1-2 drops of Silver Nitrate to 2-3 drops of 2N HCl or NaCl solution. Add concentrated Ammonia up to complete dissolving. Add by drops solution of Nitrate acid up to precipitate formation.

All indicated reactions are performed in one test-tube.

3.9.2. Characteristic reactions of Bromide anions Br^-

1. Chloric water Cl_2 (*it is the solution of Cl_2 in H_2O*). Cl_2 reacts with bromides displacing free bromine from its salts:

$$2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$$

For example,

$$2KBr + Cl_2 \rightarrow Br_2 + 2KCl.$$

Test carrying out

Add 5-6 drops of benzol and 4-5 drops of chloric water to 6-8 drops of bromine salt solution (Potassium or Sodium bromide). Shake the contents of the test-tube. The isolated Bromine is better dissolved in benzol than in H_2O and benzol layer becomes yellow.

3.9.3. Characteristic reactions of Iodide anions I^-

1. Chloric water Cl_2 (*it is the solution of Cl_2 in H_2O*). The reaction is performed in the same way as previous one (Br^- ions with chloric water). Benzol layer is colored in pink or crimson:

$$2I^- + Cl_2 \rightarrow 2Cl^- + I_2$$

For example,

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

In excess of chloric water color may vanish due to oxidation of free I_2 to Iodate (V) acid HIO_3:

$$I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl.$$

Test carrying out

Add 5-6 drops of benzol and 4-5 drops of chloric water to 6-8 drops of iodine salt solution (Potassium or Sodium Iodide). Shake the contents of the test-tube. The isolated Iodine is better dissolved in benzol than in H_2O and benzol layer becomes pink or crimson.

2. Copper salts (for example, Copper Sulfate *$CuSO_4$*) react with I^- according to equation:

$$2CuSO_4 + 4KI = 2CuI\downarrow + I_2 + 2K_2SO_4$$

$$\begin{array}{l|l} Cu^{2+} + 1\bar{e} \rightarrow Cu^{1+} & 2 \\ 2I^- - 2\bar{e} \rightarrow I_2 & 1 \end{array}$$

CuI is a milk-white precipitate. But free Iodine colored this precipitate in brown color.

3.10. The third group of anions

There is no group reagent in consequence of solubility of the most salts with nitrate, nitrite and acetate anions.

3.10.1. Characteristic reactions of Nitrite anions NO_2^-

1. Potassium Iodide *(KI)*. Potassium iodide is oxidized in acetous medium by nitrite ions up to free I_2:

$$2NO_2^- + 2I^- + 4CH_3COOH = I_2 + 2NO + 4CH_3COO^- + 2H_2O.$$

For example,

$$2KNO_2 + 2KI + 4CH_3COOH = I_2 + 2NO + 4CH_3COOK + 2H_2O$$

$$\begin{array}{l|l} N^{3+} + 1\bar{e} \rightarrow N^{2+} & 2 \\ 2I^- - 2\bar{e} \rightarrow I_2 & 1 \end{array}$$

Presence of free Iodine may be determined by adding of starch. Starch is very sensitive and specific indicator for Iodine.

Test carrying out

Add 1 drop of fresh-prepared starch, 2 drops of 2 N Acetic acid, 1 drop of 2N Potassium Iodide KI to 2-3 drops of Sodium or Potassium Nitrite ($NaNO_2$ or KNO_2). Observe color of mixture.

2. Potassium Permanganate (*$KMnO_4$*). In acid medium $KMnO_4$ oxidizes the nitrite ions up to nitrate ions. The color of $KMnO_4$ disappears and the solution becomes colorless:

$$5NO_2^- + 2MnO_4^- + 6H^+ = 5NO_3^- + 2Mn^{2+} + 3H_2O.$$

For example,

$$5KNO_2 + 2KMnO_4 + 3H_2SO_4 = 5KNO_3 + 2MnSO_4 + K_2SO_4 + 3H_2O$$

$$\begin{array}{l|l} N^{3+} - 2\bar{e} \rightarrow N^{5+} & 5 \\ Mn^{7+} + 5\bar{e} \rightarrow Mn^{2+} & 2 \end{array}$$

Test carrying out

Add 1-2 drops of Potassium Permanganate $KMnO_4$, 1-2 drops of 2N Sulfate Acid H_2SO_4 to 2-3 drops of Sodium or Potassium Nitrite ($NaNO_2$ or KNO_2).

3. Strong acids decompose Nitrites with formation of gaseous brown NO_2:

$$2NO_2^- + 2H^+ = 2HNO_2;$$

$$2HNO_2 = NO_2\uparrow + NO\uparrow + H_2O.$$

For example,

$$2NaNO_2 + H_2SO_4 = Na_2SO_4 + 2HNO_2.$$

Test carrying out

Add 2-3 drops of 2N Sulfate acid H_2SO_4 to 2-3 drops of Sodium or Potassium Nitrite ($NaNO_2$ or KNO_2).

3.10.2. Characteristic reactions of Nitrate anions NO_3^-

1. Iron (II) Sulfate ***($FeSO_4$)*** (in excess) in presence of concentrated sulfate acid H_2SO_4 reacts with nitrates with formation of complex compound $[Fe(NO)]SO_4$. The reaction is called "brown ring":

$$2NaN^{5+}O_3+6Fe^{2+}SO_4+4H_2SO_4=3Fe_2^{3+}(SO_4)_3+2N^{2+}O+Na_2SO_4+4H_2O$$

$$\begin{array}{l|l} 2Fe^{2+} - 2\bar{e} \rightarrow 2Fe^{3+} & 3 \\ N^{5+} + 3\bar{e} \quad \rightarrow N^{2+} & 2 \end{array}$$

$$NO + FeSO_4 = [Fe(NO)]SO_4$$

Test carrying out

Add 4-5 drops of saturated solution of Iron (II) Sulfate $FeSO_4$ to 4-5 drops of $NaNO_3$ or KNO_3, shake mixture. The concentrated sulfate acid should be carefully dropped at the test-tube wall (in bending state) in order not to mix the solution in the test-tube. Slowly lift test-tube in vertical state. Observe forming of “brown ring”.

Be careful in the process of reaction performance *(concentrated Sulfate acid!).*

3.10.3. Characteristic reactions of Acetate anions CH_3COO^-

1. Strong acids. At HCl or H_2SO_4 action to acetates free acetic acid is isolated which can be identified by odor:

$$CH_3COO^- + H^+ = CH_3COOH\uparrow.$$

For example,

$$2CH_3COONa + H_2SO_4 = Na_2SO_4 + 2CH_3COOH\uparrow.$$

Test carrying out

Add 3-4 drops of Sulfate acid H_2SO_4 to 5-6 drops of Sodium Acetate CH_3COONa, heat mixture.

2. Iron (III) Chloride ***($FeCl_3$)*** with solution of Acetate forms red-brown solution of Iron (III) Acetate:

$$FeCl_3 + 3CH_3COONa = Fe(CH_3COO)_3 + 3NaCl.$$

When this solution is diluted and heated, the precipitate of basic salt formed due to intensification of hydrolysis:

$$Fe(CH_3COO)_3 + 2H_2O = Fe(OH)_2CH_3COO\downarrow + 2CH_3COOH.$$

Test carrying out

Add 1-2 drops of $FeCl_3$ solution to 5-6 drops of Sodium Acetate. Observe color of solution. Add 4-6 mL of water and heat mixture on water bath up to forming of red-brown precipitate.

3.11. Analysis of mixture of cations of I-IV analytical groups

Qualitative analysis of cation mixture consists of several necessary stages:

1. Previous researches;
2. Fractional analysis for presence of certain types of some cations;
3. Systematic analysis of cation mixture.

Previous researches

Before beginning of the analysis it is necessary to define the color of solution of examined mixture, smell and reaction of medium. For example, colorless solution testifies to absence of number of cations which influence the solution coloring:

Cu^{2+} - dark blue, blue, green-and-blue;
Co^{2+} - pink;
Ni^{2+} - light green;
Fe^{3+} - yellow-and-brown

Alkali medium of the examined mixture may testify to presence of cations of K^+, Na^+, Ca^{2+}, Sr^{2+}, which give hydrolytically alkali salts. Odor can be provided only by ammonium salts. But all these assumptions have to be checked in process of the analysis.

Fractional analysis

By fractional analysis from the mixture of cations one can determine only those cations which are opened by specific reactions: NH_4^+, Na^+, Fe^{2+}, Fe^{3+}, Mn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}. These reactions are performed in separate portions of solution, the order of systematic analysis being adjusted according to the results obtained.

Systematic analysis

Systematic analysis is appropriate to begin reactions with group or selective reagents to presence of certain group of cations or some cations in the group. In case of positive result one observes the reaction of separation, while in case of positive one - this stage of analysis is missing. Reactions are performed by drop method (up to 8-10 drops), while operations of separation - in reagents’ volume of 2-4 mL. Solutions are heated in water bath. Determination and separation of cations’ groups begin with the last group.

3.12. Order of fractional and systematic analysis of cations' mixture of I-IV analytical groups

3.12.1. Fractional analysis

1. Test for NH_4^+: Add 10-12 drops of concentrated solution of NaOH (to pH=10-12) to 6-8 drops of the examined mixture and the obtained solution heat on water bath. Isolated ammonia is detected on odor or red litmus paper wetted by DW, which becomes blue in ammonia vapor.

2. Test for Na^+: Add 1-2 drops of DW and 3-5 drops of Zinc-Uranyl-Acetate $Zn(UO_2)_3(CH_3COO)_8$ to 4-6 drops of the examined mixture; wait a few minutes. In presence of Na^+ ions it isprecipitated light green-yellow crystalline sediment.

3. Test for Fe^{2+}: Add 1-2 drops of 2N CH_3COOH (pH~3-5) and 3-5 drops of $K_3[Fe(CN)_6]$ to 4-5 drops of the examined mixture. In presence of Fe^{2+} precipitates dark-blue sediment of Turnbull's blue.

4. Test for Fe^{3+}: Add 1-2 drops of HCl (pH=2-3) and 3-5 drops of $K_4[Fe(CN)_6]$ to 4-5 drops of the examined mixture. In presence of Fe^{3+} precipitates blue sediment of Prussian blue.

5. Test for Cu^{2+}: Add 10-15 drops of concentrated NH_4OH to 4-5 drops of the examined mixture; wait a few minutes (there may be some sediment). In presence of Cu^{2+} the upper solution colored in deep-blue color.

6. Test for Co^{2+}:

Variant A. It is realized **in presence** of Fe^{3+} (see p. 4): Add some grains of NaF to 6-8 drops of the examined mixture; mix tube content till complete solve of solid phase, and then add 2-3 drops of solution NH_4SCN saturated in acetone (if the solution is red, one should add NaF till the red color disappears). If the blue color solution is observed - there is Co^{2+}.

Variant B. It is realized **in absence** of Fe^{3+} (see p. 4): Add 6-8 drops of the examined mixture to 2-3 drops of NH_4SCN solution saturated in acetone. if blue color of solution, then there is Co^{2+} .

7. Test for Mn^{2+} : Add 10-12 drops of 2N HNO_3 and a few grains of $NaBiO_3$ To 1-2 drops of the examined mixture. The mixture is left for 2-3 minutes; if crimson color of solution observed, then there is Mn^{2+}, (it could appear light pink coloring in the presence of Fe^{2+} - the trace of Mn^{2+} presents).

8. Test for Ni^{2+}:

Variant A. It is realized **in absence neither Fe^{3+} or Cu^{2+}**: Add 10-15 drops of concentrated NH_4OH to 6-8 drops of the examined mixture, shuffle tube content and add 2-3 drops of Dimethylglioxime (Chugaev's reagent) $C_4H_8N_2O_2$; if crimson colored sediment formed, then there is Ni $^{2+}$.

Variant B. It is realized **in presence of Fe^{3+}**: Add a few grains of NaF up to complete solving, and then 10-12 drops of concentrated NH_4OH and 2-3 drops of Dimethylglioxime; if crimson colored sediment, then there is Ni^{2+} to 6-8 drops of the examined mixture.

Variant C. It is realized **in presence of Cu^{2+}**: Add 3-4 drops of diluted CH_3COOH to 6-8 drops of the examined mixture and then 5-6 drops of KI solution and the sediment is separated by centrifuge; add to brown supernatant liquid by drops $Na_2S_2O_3$ till the solution gets colorless, then one should add 10-15 drops of NH_4OH and 2-3 drops of Dimethylglioxime; if crimson colored sediment observed, then there is Ni^{2+}.

Variant D. It is realized **in presence of Fe^{3+} and Cu^{2+}** at the same time: Then firstly Co^{2+} is separated as described above in the Variant C, and then Fe^{3+} in supernatant liquid is masked by adding NaF as in the variant |B and proceed as has been described above.

Variant E. It is realized **in presence of Fe^{2+}**, it is oxidized by 2-3 drops of the 3% solution of H_2O_2 to Fe^{3+}, and then - as has been described above in the variant B.

3.12.2. Systematic analysis

9. Test for K^+:

Variant A. It is realized **in absence of NH_4^+ and Cu^{2+}:** Add by drops 1-2 mL of saturated solution of Na_2CO_3 to 1-2 mL of the examined mixture (in centrifugal test-tube); the mixture is centifugated, supernatant liquid is tested for fullness of sediment. Then one should add 1-2 drops of CH_3COOH to pH = 6, to the obtained solution one adds 5-6 drops of $Na_3[Co(NO_2)_6]$; if there is yellow-orange sediment - then there is K^+.

Variant B. It is realized **in presence of NH_4^+, but absence of Cu^{2+}:** Add by drops 2-3 mL of saturated solution of Na_2CO_3 to 2-3 mL of the examined mixture (in centrifugal test-tube); the mixture is centifugated, supernatant liquid is tested for fullness of sediment. The filtrate is carried into the crucible, evaporate it on the gas burner, and then calcinate it in muffle during 1,5 hours at temperature 700-800°C. After then it is necessary to control the fullness of ammonia evaporation. Add 10 drops of DW and 1-2 drops of Nessler's reactant to a few crystals of dry residue transport in clean test-tube,. If reddish precipitation was absent, ammonia was evaporated completely. A main part of the dry residue in crucible is being solved in 10-15 drops of DW. Then one should add 1-2 drops of

CH_3COOH to pH = 6, to the obtained solution one adds 5-6 drops of $Na_3[Co(NO_2)_6]$; if there is yellow-and-orange sediment - then there is K^+.

Variant C. It is realized **in absence of NH_4^+, but presence of Cu^{2+}:** Add 7-10 drops of solution of NaI, and the sediment obtained is separated using centrifuge (don't forget test of fullness of precipitate!) to 1-2 mL of the examined mixture in centrifugal test-tube; the supernatant solution has to be decanted in clean test-tube. Then $Na_2S_2O_3$ is added till the solution gets colorless, and then – as has been described above (from the start of Variant A: Add Na_2CO_3 and so on).

10. Separation and analysis of cations of the 4th group (Ag^+ and Pb^{2+}).

Add 2 drops of 2N HCl; if there is sediment, then cations of the 4th group are present and must be separated from the examined mixture solution as follows to 2-3 drops of the examined mixture: add 2-3 mL of 10% HCl to 2-3 mL of the examined mixture; the sediment obtained is separated using centrifuge (don't forget test of fullness of precipitate!); **The Filtrate 1** (**safe it in the separate labeled tube for the next analysis**) obtained is decanted into clean test-tube, and in the solid residue **- Sediment 1** Ag^+ and Pb^{2+} have to be determined. To do this the **sediment 1** in centrifuge test-tube is rinsed with 2-3 mL of distilled hot water and is centrifuged again (for separating of $PbCl_2$ soluble in hot water), which gives us **the Filtrate 2** and the **Sediment 2.** The filtrate 2 is decanted into the clean test-tube; then 3-4 drops of the solution KI should be added. If yellow sediment, then there is Pb^{2+}.

If there is **the sediment 2** in the centrifuge test-tube, it should be processed by adding 2-3 mL of concentrated solution of NH_4OH and centrifuged again. **The Filtrate 3** is decanted in a clean test-tube; then the solution 2N HNO_3 to pH = 3-4 is added (using the universal litmus indicator). If the turbidity or bulky white precipitation observes, then there is Ag^+.

11. Separation and analysis of cations Ca^{2+} and Sr^{2+}.

Variant A. It is realized **in absence of cations of the 4th group (Ag^+ and/or Pb^{2+}).** Add 2-3 drops of 20% H_2SO_4 and 2-3 drops of acetone (or alcohol) to 3-5 drops of examined mixture. If there is sediment, then there is Ca^{2+} and Sr^{2+}. If the solution remains clean, then there is no Ca^{2+} and Sr^{2+}.

If the precipitation was observed, it is necessary to determine what cations are present: Ca^{2+} and Sr^{2+} together, either Ca^{2+} or Sr^{2+} separately. To do this to 2-3 mL of the examined mixture add 1-2 mL of 20% H_2SO_4 and

5-10 drops of acetone. Content of test-tube should be mixed and heated for 3-4 minutes (to 70-80°C). The mixture with the sediment is cooled down, and centrifuged. There is **the Sediment 4** and **the Filtrate 4** (**safe it in the separate labeled tube for the next analysis**). Don't forget test of fullness of precipitate! Add 1-2 mL of concentrated or saturated solution of $(NH_4)_2SO_4$ and then heat it to the sediment 4 in centrifuge test-tube. If the sediment is left, then it should be centrifuged again. Decant **the Filtrate 5** in clean test-tube, add NH_4OH to pH ~ 5-6 (by universal litmus indicator) and add 5-6 drops of $(NH_4)_2C_2O_4$. If there is white sediment, then there is Ca^{2+}.

Determination of Sr^{2+}: 1 mL of saturated solution of $(NH_4)_2SO_4$ is heated in test-tube, and then add 10-12 drops of the examined mixture. If there is sediment, then there is Sr^{2+} .

Variant B. It is realized **in presence of cations of the 4th group (Ag^+ and/or Pb^{2+})** like the Variant A with only one difference – examined mixture is replaced by the Filtrate 1.

12. Separation and analysis of cations Al^{3+} and Zn^{2+}.

Variant A. It is realized **in the absence of the 4th group (Ag^+ and/or Pb^{2+}), Ca^{2+} and Sr^{2+}.**

Add 5-10 drops of 10% H_2O_2 to 1-2 mL of the examined mixture one should (if there is Mn^{2+}, see 3.12.1. Fractional analysis, point 7) and 2-3 mL of 10% NaOH to pH ~ 12-14 (strongly alkali medium) and heat on the water bath for 4-5 minutes. After cooling this mixture is decanted in centrifuge test-tube and should be centrifuged, **the sediment 6** (useless) and **the filtrate 6** should be separated.

In the filtrate 6 one should define the presence of ions of Zn^{2+} and Al^{3+} (in the form of anions ZnO_2^{2-} and AlO_3^{3-}).

Determination of Al^{3+}: Add a few crystals of NH_4Cl till getting the saturated solution to 7-10 drops of **the filtrate 6**. The test-tube with the solution is heated on the water bath (for 4-5 minutes). If there is Al^{3+} there must be white amorphous sediment $Al(OH)_3$.

Determination of Zn^{2+}: Add (to pH~5 by universal litmus paper) and 5-6 drops of $K_3[Fe(CN)_6]$ to 7-10 drops of the filtrate 6. If there is yellow-and-orange sediment, then there is Zn^{2+}.

Variant B. It is realized **in the presence of the 4th group (Ag^+ and/or Pb^{2+}) but absence of Ca^{2+} and Sr^{2+}** like the Variant A with only one difference – examined mixture is replaced by the Filtrate 1.

Variant C. It is realized **in the presence of the 4th group (Ag^+ and/or Pb^{2+}), Ca^{2+} and/or Sr^{2+}** like the Variant A with only one difference

– examined mixture is replaced by corresponding volume of the Filtrate 4 prepared in the Variant B, p. 11.

13. Separation and analysis of cation Mg^{2+}

Variant A: It is realized **in the presence of Cu^{2+}** in the examined mixture, then 8-10 drops of NaI are added to 1 mL of the examined mixture in centrifuge test-tube. The sediment obtained should be centrifuged: there are the sediment and **the filtrate 7.**

To **the filtrate 7** in a clean test-tube one should add 3-4 drops of $Na_2S_2O_3$ till the solution gets colorless, then one should add 7-10 drops of the solution NH_4Cl, 5-6 drops of concentrated NH_4OH and 15-20 drops of concentrated $(NH_4)_2CO_3$. The mixture then should be heated on the water bath, decant in centrifuge teat-tube and centrifuged. The sediment and **the Filtrate 8** are obtained. Add 5-6 drops of Na_2HPO_4 to the filtrate 8 decanted in a clean test-tube one should. Formation of white sediment indicates the presence of ions of Mg^{2+}.

Variant B: It is realized **in the absence of Cu^{2+}** in the examined mixture: NH_4OH, NH_4Cl and $(NH_4)_2CO_3$ are added to 1 mL of the examined mixture and then according to procedure described above in the Variant A.

Results of this experimental work is presented in the form of protocol of Analysis.

EXAMPLE OF PROTOCOL OF ANALYSIS

Content of operation	**Visual effect**	**Conclusion**
1	2	3
1. Predefinition		
A. Color of solution	Your result	Previous hypothesis about presence or absence of colored ions (Fe^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}) in examined mixture

1	2	3
B. Odor	Your result	Previous hypothesis about presence or absence of NH_4^+ ions
C. pH of solution	Your result	Previous hypothesis about presence or absence of ions of weak bases (NH_4^+, Fe^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Al^{3+}, Zn^{2+}, Mg^{2+}) in the case of pH less than 7.
2. Fractional analysis		
1. Test for NH_4^+: Add 10 drops of concentrated solution of NaOH (to pH=12) and the obtained solution heat on water bath to 6 drops of the examined mixture.	Your result	Present or absent **NH_4^+** in examined mixture
2. Test for Na^+: Add 2 drops of DW and 3 drops of Zinc-Uranyl-Acetate $Zn(UO_2)_3(CH_3COO)_8$ to 4 drops of the examined mixture.	Your result	Present or absent **Na^+** in examined mixture
3. Test for Fe^{2+}: Add 2 drops of 2N CH_3COOH (pH~5) and 3 drops of $K_3[Fe(CN)_6]$ to 4 drops of the examined mixture.	Your result	Present or absent **Fe^{2+}** in examined mixture
4. Test for Fe^{3+}: Add 2 drops of HCl (pH~3) and 3 drops of $K_4[Fe(CN)_6]$ to 4 drops of the examined mixture.	Your result	Present or absent **Fe^{3+}** in examined mixture
5. Test for Cu^{2+}: Add 10 drops of concentrated NH_4OH to 4 drops of the examined mixture.	Your result	Present or absent **Cu^{2+}** in examined mixture

1	2	3
6. Test for Co^{2+}: Select Variant A or Variant B according to result of p. 4.	Your result	Present or absent **Co^{2+}** in examined mixture
7. Test for Mn^{2+}: Add 10 drops of 2N HNO_3 and a few grains of $NaBiO_3$ to 2 drops of the examined mixture.	Your result	Present or absent **Mn^{2+}** in examined mixture or observe trace quantities of this ion
8. Test for Ni $^{2+}$: Select Variant A or B or C or D, or E according to result of pp. 3, 4, 5 and 6.	Your result	Present or absent **Ni^{2+}** in examined mixture
3. Systematic analysis		
9. Test for K^+: Select Variant A or Variant B according to results of pp. 1, 5.	Your result	Present or absent **K^+** in examined mixture
10. Separation and analysis of cations of the 4th group (Ag^+ and Pb^{2+}): Add 2 drops of 2N HCl to 2 drops of the examined mixture. The next order of analysis – depends on result of this step.	Your result	Present or absent **Ag^+ and/or Pb^{2+}** in examined mixture
11. Separation and analysis of cations Ca^{2+} and Sr^{2+}: Select Variant A or B according to result of p. 10.	Your result	Present or absent **Ca^{2+} and/or Sr^{2+}** in examined mixture
12. Separation and analysis of cations Al^{3+} and Zn^{2+}: Select Variant A or B or C according to results of p. 10 and 11.	Your result	Present or absent **Al^{3+} and/or Zn^{2+}** in examined mixture
13. Separation and analysis of cation Mg^{2+}: Select Variant A or B according to result of p. 5.	Your result	Present or absent **Mg^{2+}** in examined mixture

GENERAL CONCLUSION: In examined mixture it was discovered cations (note your results).

Teacher examines your result. If it was detected mistakes, analysis must be repeated and description of additive stages and right results should be add to the protocol.

3.13. Analysis of unknown substance

Background

Unlike covalent compounds, which can be identified using physical properties like boiling point and refractive index, ionic compounds are more appropriately identified with their chemical properties. In the qualitative analysis procedure, the chemical properties of an unknown substance are determined by systematically reacting the unknown with a number of different reagents.

By predetermining what the particular reaction will produce if a specific ion is present, the ions that actually are in the solution can be identified. For example, if a reaction is known to produce a precipitate if ion A is present and a precipitate is formed when the reaction is run, then ion A may be present in solution (there may be, and usually are, other ions that will also precipitate with a particular reagent). If no precipitate is formed when the reaction is run, then ion A is clearly not present in the unknown solution and a different reaction will have to be run to determine what ions are present.

There are two general situations in which qualitative analysis is used - in the identification of a simple salt, or the identification of multiple cations in a solution.

3.13.1. Identifying a Simple Salt by logistics way

The basic testing procedure for identifying a salt is as follows.

1. Appearance of compound

The compound will most likely be in solid form. Note the color and shape of the crystals. Ionic compounds formed from the representative elements tend to be white or colorless, while ions of transition elements tend to be colored. The following is a table of the colors of metal ions in solution with NO_3^-.

Ion	Color
Co^{2+}	Rose
Co^{3+}	Violet
Cr^{3+}	Violet
Cu^{2+}	Blue
Fe^{2+}	Pale green, pale violet
Fe^{3+}	Yellow-brown
Mn^{2+}	Pale pink
Ni^{2+}	Blue-green

2. Heating effect

Heating a compound can cause a liquid to condense on the inside of the test tube. This is probably water, indicating that the compound is a hydrate. If a gas is given off, note the color and odor of the gas. The nitrate, carbonate, and sulfite ions may decompose, as illustrated by the reactions:

$$2Pb(NO_3)_2(s) + \text{heat} \rightarrow 2\ PbO(s) + O_2(g) + 4\ NO_2\ (g, \text{brown})$$

$$CaCO_3(s) + \text{heat} \rightarrow CaO(s) + CO_2\ (g, \text{colorless, odorless})$$

$$CaSO_3(s) + \text{heat} \rightarrow CaO(s) + SO_2\ (g, \text{colorless, pungent})$$

Some bromides and iodides decompose to give Br_2 (g, orange-brown) and I_2 (g, purple).

3. Flame test

Solutions of ions, when mixed with concentrated HCl and heated on a nickel/chromium wire in a flame, cause the flame to change to a color characteristic of the atom. Visible colors occur with the following ions:

Sodium	Bright yellow (intense, persistent)
Potassium	Pale violet (slight, fleeting)
Calcium	Brick red (medium, fleeting)
Strontium	Crimson (medium)
Barium	Light green (slight)
Lead	Pale bluish (slight, fleeting)
Copper	Green or blue (medium, persistent)

4. Solubility in water

Place one small spatula of the compound in 1 mL of water. If the compound is soluble this amount will dissolve after considerable stirring. If the compound is moderately soluble, some of this amount will dissolve. If the compound is insoluble, even a very small amount will not dissolve.

General solubility rules:

1. All nitrates are soluble.
2. Practically all sodium, potassium, and ammonium salts are soluble.
3. All chlorides, bromides, and iodides are soluble except those of silver, mercury(I), and lead(II).
4. All sulfates are soluble except those of strontium, and lead(II), which are insoluble, and those of calcium and silver which are moderately soluble.
5. All carbonates, sulfites, and phosphates are insoluble except those of sodium, potassium, and ammonium.
6. All hydroxides are insoluble except those of the alkali metals. The hydroxides of calcium, strontium are moderately soluble. Ammonium hydroxide does not exist; ammonium hydroxide is a misnomer for aqueous ammonia, NH_3 (aq).

5. Reaction with nitrate acid

Add nitrate acid to the compound and observe any reaction that occurs. If the compound dissolved in water, it should dissolve in nitrate acid. If it did not dissolve in water, but appears to be dissolving in nitrate acid, it is undergoing a chemical reaction. In general, compounds that contain anions that are the conjugate bases of weak acids will react (unless the compounds are very insoluble). For example:

$$CaCO_3(s) + 2\,H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l) + CO_2\,(g, \text{colorless, odorless})$$

$$Ca_3(PO_4)_2(s) + 6\,H^+(aq) \rightarrow 3\,Ca^{2+}(aq) + 2\,H_3PO_4\,(aq)$$

The remaining tests must be performed on a solution of the compound.

If the compound is insoluble in water, dissolve it in nitrate acid. Otherwise, dissolve in water.

6. Reaction with sodium hydroxide

Add NaOH dropwise to the solution, stir or shake the solution, and observe any reaction (if the compound was dissolved in nitrate acid, the first several drops will neutralize the acid so be sure to check the pH with litmus paper). Look for a precipitate (refer to the solubility rules for hydroxides). If a precipitate forms, continue adding NaOH. Some metal hydroxides are amphoteric (Al^{3+}, Zn^{2+}, Pb^{2+}) and will form a complex ion and redissolve.

7. Reaction with ammonia

Add NH_3 dropwise to the solution, stir or shake the solution, and observe any reaction. If a metal hydroxide or metal basic salt precipitate forms, continue adding ammonia. Some metal hydroxides form a complex ion and redissolve:

Acid Solution	Basic Solution	Solution with Excess NH_3	Color of Complex
$Ni^{2+}(aq)$	$Ni(OH)_2(s)$	$[Ni(NH_3)_6]^{2+}(aq)$	Violet
$Cu^{2+}(aq)$	$Cu(OH)_2(s)$	$[Cu(NH_3)_4]^{2+}(aq)$	Blue
$Zn^{2+}(aq)$	$Zn(OH)_2(s)$	$[Zn(NH_3)_4]^{2+}(aq)$	Colorless
$Ag^{+}(aq)$	$Ag_2O(s)$	$[Ag(NH_3)_2]^{+}(aq)$	Colorless

8. Reaction with hydrochloric acid

Add HCl dropwise until solution tests acidic to litmus paper and observe any reaction. A precipitate will form with any cation that forms an insoluble chloride (refer to the solubility rules). For example:

$$Pb^{2+} + 2Cl^{-} \rightarrow PbCl_2(s)$$
$$Ag^{+} + Cl^{-} \rightarrow AgCl\ (s)$$

9. Reaction with sulfate acid

Add H_2SO_4 dropwise until solution is acidic and observe any reaction. A precipitate will form with any cation that forms an insoluble sulfate (refer to the solubility rules). For example:

$$Sr^{2+} + SO_4^{2-} \rightarrow SrSO_4(s)$$

10. Reaction with silver nitrate

Add HNO_3 dropwise until solution is acidic (unless of course it was dissolved in nitrate acid), then add a few drops of $AgNO_3$ and observe any reaction. A precipitate will form with certain cations that form insoluble silver compounds, but because of the acidic environment, some insoluble silver salts (e.g. salts containing CO_3^{2-}, SO_3^{2-}, and PO_4^{3-} ions) are "destroyed." Cl^{-}, Br^{-}, and I^{-} form insoluble compounds, while SO_4^{2-} forms a moderately insoluble compound.

$$Ag^{+} + Cl^{-} \rightarrow AgCl(s)$$

11. Reaction with barium chloride

Add HNO_3 dropwise until solution is acidic, boil the solution for two minutes, and then test with litmus paper. Continue adding and boiling until solution remains acidic after boiling. Cool the solution and add a few drops of $BaCl_2$ and observe any reaction. A precipitate will form with anions that form an insoluble barium compound (except the ones destroyed by acid as in the above test).

12. Specific Tests

Sometimes the above tests can not definitively confirm the presence of a specific ion. In these cases, it is necessary to do specific tests for a particular ion.

Example Unknown Salts

Sample 1 had the following characteristics:

1. Visual test: white crystalline powder;
2. Heat test: brown gas given off;
3. Flame test: no color identified;
4. Solubility in water: soluble;
5. Nitrate acid: soluble;
6. Hydroxide: formed an insoluble white precipitate, then dissolved with excess NaOH;
7. Ammonia: formed an insoluble white precipitate which did not redissolve in excess NH_3;
8. Hydrochloric acid: formed an insoluble white precipitate.

Analysis of observations:

- The brown gas given off during the heat test indicates presence of the NO_3^- ion, since the NO_3^- ion reacts to form brown NO_2 gas as shown below:

$$2Pb(NO_3)_2(s) + \text{heat} \rightarrow 2PbO(s) + O_2(g) + 4NO_2\uparrow (g)$$

- The white precipitate which formed and then redissolved with the addition of sodium hydroxide indicates the presence of an amphoteric cation. The possibilities are Al^{3+}, Pb^{2+} or Zn^{2+}. The reaction occurs as follows:

$$Al^{3+}(aq) + 3\ OH^-(aq) \rightarrow Al(OH)_3(s)$$

$$Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq).$$

- Since the cation does not form an ammonia complex, it eliminates Zn from the list of possible cations established above.
- There are only two cations which form precipitates with hydrochloric acid, Pb^{2+}, and Ag^+. Of these two, only Pb^{2+} is amphoteric. The reaction with chloride occurs as follows:

$$Pb^{2+} + 2\ Cl^- \rightarrow PbCl_2(s)$$

Conclusion: Sample 1 is $Pb(NO_3)_2$.

Sample 2 had the following characteristics: visual test: yellow/brown solid;

1. Heat test: no reaction;
2. Flame test: no reaction;
3. Solubility in water: soluble;
4. Nitrate acid: soluble;
5. Sodium hydroxide: formed an insoluble white precipitate which did not redissolve in excess NaOH;
6. Ammonia: formed an insoluble white precipitate which did not redissolve in excess NH_3;
7. Hydrochloric acid: no reaction;
8. Specific Iron (III) test (formation of a thiocyanate complex): solution turned blood red.
9. Silver nitrate: formed an insoluble white precipitate;
10. Specific chloride, bromide, iodide test: precipitate dissolved with addition of 6M ammonia.

Analysis of observations:

- The color of the solid is characteristic of the Fe^{3+} ion.
- Since the compound forms an insoluble precipitate with hydroxide, it eliminates the alkali metals, calcium and strontium. Since the cation is not amphoteric, it also eliminates aluminum, lead and zinc.
- The cation does not form an ammonia complex, which eliminates nickel, Copper (II) and silver.
- Since there is no reaction with Cl^-, the ions which have not been eliminated (Fe^{3+}, Mn^{2+}, Bi^{2+}), Fe^{3+} is the most likely. A specific ion test is needed to confirm the presence of Fe^{3+}.
- The red solution produced by the Iron (III) test confirms the presence of Iron (III). The reaction occurs as follows:

$$Fe^{3+}(aq) + 6SCN^-(aq) \rightarrow [Fe(SCN)_6]^{3-}(aq).$$

- The precipitate formed by the addition of silver nitrate indicates the presence of either chloride, bromide, or iodide. Although the colors are different (AgCl white, AgBr cream, AgI yellow), they are difficult to distinguish and a specific ion test is needed to determine which one is present.
- The specific ion test indicated that the anion present is Cl^-. The reaction occurs as follows:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$
$$AgCl(s) + 2\ NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$$

Conclusion: Sample 2 is $FeCl_3$

3.13.2. Identifying a Simple Salt by step-by-step way

Unknown substance is considered as the salt soluble in water and it consists of one cation and one anion. Search for cation and anion leads to the first positive reaction.

Qualitative analysis of unknown substance consists of series of operations:

a) Predefinition;
b) Cation definition;
c) Anion definition.

A. Predefinition

Draw attention to color, as described above, part 3.13.1, p.1. configuration and size of particles.

Draw attention to odor of substance. Ammonium- and acetate-contained salts have a characteristic odor.

Dilution of unknown substance

The tests for dilution of the substance are started from the processing of some quantity of its grains by DW firstly in cold but if necessary at heating.

The most of the substances, which are taken for the analysis, are easily dissolved in water or in diluted hydrochloric acid.

In our case the unknown substance is soluble in water or is the solution.

a) If the received sample is the solid substance, so 0,15 - 0,2 g of substance is dissolved in 6-8 mL of DW (if necessary the solution is heated in water bath);

b) If the received sample is the solution, so it should be diluted: 3-4 mL of DW are added to 1 mL of solution.

pH of received solution is determined. Acid reaction of solution indicates that the sample can be the salt of weak base and strong acid ($AlCl_3$, NH_4Cl, $Zn(NO_3)_2$). Alkali reaction of the solution is the salt of weak acid and strong base (Na_2CO_3, K_3PO_4, CH_3COONa). The neutral reaction of the solution indicates that the substance is the salt of strong acid and strong base or weak acid and weak base (KCl, Na_2SO_4, $CaCl_2$, CH_3COONH_4).

The determination of cations and anions starts after the definition of medium reaction. The analysis is carried out up to the first positive reaction.

B. Determination of cations

1. Test for the presence of IV group of cations

Add the group reagent HCl to separate portion of the examined solution. If precipitation is formed so the cation belongs to IV group. It may be Ag^+ or Pb^{2+}.

Special test of Ag^+ - to precipitate formed of HCl, add concentrated NH_3. If precipitate dissolved completely, add nitrate acid by drops till turbidity;

Special test of Pb^{2+} - with KI and subsequent re-crystallization of "gold rain".

2. Test for the presence of III and II groups of cations

Add the group reagent $(NH_4)_2HPO_4$ to separate portion of the solution. If precipitation is formed so the cation can belong to III or II group. In this case add some drops of concentrated NH_4OH (or excess of 10% NH_4OH) to the received precipitation. If we see that:

The precipitation is dissolved, so the cation belongs to the III group; if the precipitation is not dissolved so the cation belongs to the II group.

Variant A. The precipitation is dissolved - cation of the III group; the reactions are performed in separate portions of the solution:

Special test of Cu^{2+} - with NH_4OH (excess);

Special test of Zn^{2+} - with $K_3[Fe(CN)_6]$;

Special test of Co^{2+} - with NH_4SCN in acetone;

Special test of Ni^{2+} - with of Dimethylglioxime (Chugaev's reagent) $C_4H_8N_2O_2$.

Variant B. If the precipitation is not dissolved - II group of cations:

Special test of Fe^{2+} - with $K_3[Fe(CN)_6]$;

Special test of Fe^{3+} - with $K_4[Fe(CN)_6]$ or NH_4SCN;

Special test of Mn^{2+} - with $NaBiO_3 + HNO_3$ diluted;

Special test of Al^{3+} - with NaOH and crystalline NH_4Cl at heating;

Special test of Ca^{2+} - with $(NH_4)_2C_2O_4$;

Special test of Sr^{2+} - with gypsum water (saturated water solution of $CaSO_4$);

Special test of Mg^{2+} - with Na_2HPO_4 in presence of NH_4OH + NH_4Cl.

3. Determination of I group of cations

The sequence and conditions of reaction performance should be followed:

Special test of NH_4^+ - with NaOH at heating;

Special test of K^+ - with $Na_3[Co(NO_2)_6]$ or $NaHC_4H_4O_6$;

Special test of Na^+ - with Zinc-Uranyl-Acetate $Zn(UO_2)_3(CH_3COO)_8$.

C. Determination of anions

It is concluded that series of anions can be present in solution after the definition of cation, taking into account that unknown substance is soluble in water.

1. Determination of I group of anions

Add $BaCl_2$ group reagent to the separate portion of examined solution. If the precipitation is formed so the anions are of the first group. Remember, that anions $B_4O_7^{2-}$, SiO_3^{2-}, MoO_4^{2-} form precipitates only from concentrated solutions.

Special test of SO_4^{2-} - 2N HCl acts to precipitation. If the precipitation is not dissolved so SO_4^{2-} ion is present.

Special test of CO_3^{2-} - as the result of 2N HCl action to precipitation, the last is dissolved with gas bubbles isolation. To be sure of CO_3^{2-} to pass gas through acidified weak solution of $KMnO_4$ used test system (see fig. 10, p. 66). If permanganate solution keeps light-crimson, CO_3^{2-} is present.

Special test of SO_3^{2-} - as the result of 2N HCl action to precipitation, the last is dissolved with gas bubbles isolation. To be sure of SO_3^{2-} to pass gas through acidified weak solution of $KMnO_4$ used test system (see fig. 10, p. 66). If permanganate solution decolorized, SO_3^{2-} is present.

Special test of PO_4^{3-} - as the result of 2N HCl action, the precipitation is dissolved without gas isolation. It can be supposed that there is PO_4^{3-}. Then perform the reaction of PO_4^{3-} determination with molybdenum liquid at heating in the separate portion of examined solution.

Even if the result of $BaCl_2$ action the precipitation is not deposited, it is obligatory to examine the presence of $B_4O_7^{2-}$, SiO_3^{2-}, MoO_4^{2-}.

Special test of $B_4O_7^{2-}$ - flame test with ethyl alcohol;

Special test of SiO_3^{2-} - with concentrated NH_4Cl solution;

Special test of MoO_4^{2-} - with 10% H_2O_2 in presence of concentrated ammonia.

If all previous tests are negative, so there is no the first group of anions and the search should be continued in the second group of anions.

2. Determination of II group of anions

Add $AgNO_3$ group reagent to the separate portion of examined solution in presence of 2N HNO_3. If the precipitation of white (yellow-white) color is formed so the second group of anions is present in the solution.

Special test of Cl^- - if the precipitation from group reagent is dissolved in NH_4OH and as the result of 2N HNO_3 adding the precipitation becomes turbid so there is Cl^- ion.

Special test of Br^- *and* I^- - chloric water and benzol add to the solution. If benzol layer becomes yellow, Br^- is present, crimson - I^- is present.

If as the result of group reagent action the precipitation is not deposited (there is no the second group of anions), the search should be continued in the third anion group.

3. Determination of III group of anions

Perform the determination reactions in separate portions of examined solution:

Special test of NO_3^- - with saturated $FeSO_4$ + concentrated H_2SO_4;

Special test of NO_2^- - with KI + CH_3COOH;

Special test on of CH_3COO^- - with mineral acid at heating.

On the basis of obtained results the report on unknown substance analysis should be prepared and the formula of salt should be given (see Table 8 as example).

Table 8. Example of protocol of analysis

Stage of analysis	Content of operation	Conclusion
1. Predefinition	Color of salt	
	Odor	
	Solubility in water	
	pH of water solution	
2. Determination of cations	Test for the presence of IV group of cations: *Special test of* Ag^+ and so on	
	Test for the presence of III and II groups of cations (if necessary): *Special test of* Cu^{2+} and so on	
	Test of the presence of I group of cations (if necessary): *Special test of* NH_4^+ and so on	
3. Determination of anions	Test of I group of anions *Special test of* SO_4^{2-} and so on	
	Test of II group of anions (if necessary): *Special test of* Cl^- and so on	
	Test of III group of anions (if necessary): *Special test of* NO_3^- and so on	
Result: Formula of salt is …		

3.13.3. Qualitative analysis of insoluble substances and solutions

Unknown substance may be unsoluble in water or presents a solution (colored or colorless).

In the first case, the previous stage of analysis – to dissolve unknown substance.

It may be oxides, basic salts, carbonates, phospahates, silicates all alkali-earth and heavy metals. Such given substances will be considered to consist of one cation and one anion. Search for cation and anion leads to the first positive reaction. The most of such compounds are dissolved in acids or alkalies.

Test of solubility includes to study the next solvents:

- Boiled DW (for example, $PbCl_2$ is more soluble in hot water, that in cool water);
- Diluted acetic acid CH_3COOH – dissolves the carbonates (with gassing of CO_2), oxides, hydroxides;
- Diluted hydrochloric acid HCl – does not dissolve solts of silver, lead, because AgCl and $PbCl_2$ are unsoluble in water;
- Concentrated hydrochloric acid HCl – for dissolving of oxides of heavy metals, excepted silver and lead;
- Diluted nitrate acid HNO_3 – for dissolving of free heavy metals, oxides and hydroxides;
- Concentrated nitrate acid HNO_3 – for dissolving of free heavy metals, oxides and hydroxides;
- “Aqua regia” – mixture of concentrated hydrochloric acid HCl and Concentrated nitrate acid HNO_3 (in volume ratio 3:1) – for dissolving of the most unsoluble compounds.

The next order of analysis is the same described above. **Remember, that prepared solution would be acidic, if we dissolved the unknown substance in weak or strong acid**. For tests of cations and anions it is necessary to regulate pH of examined solution to add corresponding agents (for example, diluted NaOH by drops till required medium). Of course, anion of acid, used for dissolving, will present in examined solution.

In the second case, the previous stage of analysis – to determine the pH of examined solution, used universal litmus.

If medium is strong acidic (less than 2-3) – most probably, that the examined solution is acid. Remember, that the most inorganic acids (exepting silicate acid and a few others) and acetic acid are soluble in water.

If medium is strong alkaline (more than 11-12) – most probably, that the examined solution is alkali.

If medium is neutral (near 7) – most probably, that the examined solutions are water or salts formed strong base and strong acid or weak base and weak acid.

For tests of cations and anions it is necessary to regulate pH of examined solution to add corresponding agents. Remember, that components of alanytes used for regulation of pH will be detected in examined solution.

The next order of analysis is the same one as described in p. 3.13.2.

CHAPTER 4. QUNTITATIVE ANALYSIS

Vocabulary

English	Українська назва	English	Українська назва
Gravimetric analysis, gravimetry, mass analysis	Гравіметричний (ваговий) аналіз	Solubility	Розчинність
Volumetric or titrimetric analysis	Титриметричний (об'ємний) аналіз	Induction period	Період індукції
Density	Густина	Nucleation	Нуклеатизація (утворення зародків кристалів)
Refractive index	Індекс переломлення	Electric double layer	Електричний подвійний шар
Absorption	Абсорбція (поглинання)	Digestion	Дигестія (ріст кристалів)
Polarization of light	Поляризація світла	Co-precipitation	Співосадження
Magnetic susceptibility	Магнітна сприйнятливість	Occlusion	Оклюзія
Electromotive force	Електрорушійна сила	Desiccator	Ексікатор
Analytical balance	Аналітичні терези	Porcelain crucibles	Фарфорові тиглі
Dessicator	Ексікатор	Tongs	Щипці

Quantitative Chemical Analysis - branch of chemistry that deals with the determination of the amount or percentage of one or more constituents of a sample. A variety of methods is employed for quantitative analyses, which for convenience may be broadly classified as chemical or physical, depending upon which properties are utilized.

Chemical methods depend upon such reactions as precipitation, neutralization, oxidation, or, in general, the formation of a new compound. The major types of strictly chemical methods are known as gravimetric analysis (q.v.) and volumetric, or titrimetric, analysis.

Physical methods involve the measurement of some physical property such as density, refractive index, absorption or polarization of light, electromotive force, magnetic susceptibility, and numerous others. An analysis will often require a combination of methods: qualitative for separating desired constituents from a sample and quantitative for measuring the amounts present.

The basic tool in all quantitative analyses is the analytical balance, used for the accurate weighing of samples and precipitates. For usual analytical work the balance should be able to determine differences in mass of 0.1 milligram (see chapter 2.2). In microanalyses the balance must be about 1,000 times more sensitive, and, for special work, balances of even higher sensitivity have been constructed.

4.1. Chemical equilibrium in heterogeneous systems

Precipitation reactions are important in industry, medicine, and everyday life. For example, the preparation of many essential industrial chemicals such as sodium carbonate makes use of precipitation reactions.

The general rules for prediction of ionic substances solubility do not alloy to make quantitative estimation about how much of a given ionic compound will dissolve in water.

Consider a saturated solution of silver chloride that is in contact with solid silver chloride. The solubility equilibrium can be respected as

$$AgCl\ (s) \leftrightarrow Ag^{+}\ (aq) + Cl^{-}\ (aq)$$

Because salts such as AgCl are treated as strong electrolytes, all the AgCl that dissolves in water is assumed to dissociate completely into Ag^{+} and Cl^{-} ions. For heterogeneous reactions the concentration of the solid is as constant. Thus we can write the equilibrium constant for the dissolution of AgCl as

$$K_{sp} = [Ag^{+}]\cdot[Cl^{-}],$$

in which K_{sp} is called the solubility product constant or simply the solubility product. In general, **the solubility product** of a compound is the product of the molar concentrations of the constituent ions, each raised to the power of its stoichiometric coefficient in the equilibrium equation.

Other examples:

Compound	Dissociation reaction	K_{sp}
MgF_2	$MgF_2 \leftrightarrow Mg^{2+}(aq) + 2F^{-}(aq)$	$[Mg^{2+}]\cdot[F^{-}]^2$
Ag_2CO_3	$Ag_2CO_3 \leftrightarrow 2Ag^{+}(aq) + CO_3^{2-}(aq)$	$[Ag^{+}]^2\cdot[CO_3^{2-}]$
$Ca_3(PO_4)_2$	$Ca_3(PO_4)_2 \leftrightarrow 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$	$[Ca^{2+}]^3\cdot[PO_4^{3-}]^2$
$MgNH_4PO_4$	$MgNH_4PO_4 \leftrightarrow Mg^{2+}(aq) + NH_4^{+}(aq) + PO_4^{3-}(aq)$	$[Mg^{2+}]\cdot[NH_4^{+}][PO_4^{3-}]$
Bi_2S_3	$Bi_2S_3 \leftrightarrow 2Bi^{3+}(aq) + 3S^{2-}(aq)$	$[Bi^{3+}]^2\cdot[S^{2-}]^3$
$Cr(OH)_3$	$Cr(OH)_3 \leftrightarrow Cr^{3+} + 3OH^{-}$	$[Cr^{3+}]\cdot[OH^{-}]^3$

Appendix 10 lists the K_{sp} values for a number of salts and hydroxides of low solubility. Soluble salts such as NaCl and KNO_3, which have very large K_{sp} values, are not listed in the table.

For the dissolution of an ionic solid in aqueous solution, any one of the following conditions may exist:

1. The solution is unsaturated;
2. The solution is saturated;
3. The solution is supersaturated.

It may be used value **Q**, called the **ionic product**, to represent the product of the molar concentrations of the ions raised to the power of their stoichiometric coefficients. Thus for an aqueous solution containing Ag^+ and Cl^- ions at 25°C:

$$Q = [Ag^+]_0 \cdot [Cl^-]_0$$

The subscript 0 remains that these are initial concentrations and do not necessarily correspond to those at equilibrium. The possible relationships between Q and K_{sp} are:

$Q < K_{sp}$ $[Ag^+]_0 \cdot [Cl^-]_0 < 1,6 \cdot 10^{-10}$	Unsaturated solution
$Q = K_{sp}$ $[Ag^+]_0 \cdot [Cl^-]_0 = 1,6 \cdot 10^{-10}$	Saturated solution
$Q > K_{sp}$ $[Ag^+]_0 \cdot [Cl^-]_0 > 1,6 \cdot 10^{-10}$	Supersaturated solution; AgCl will precipitate out until the product of the ionic concentrations is equal to $1,6 \cdot 10^{-10}$

4.2. Molar solubility and solubility

The value of K_{sp} indicates the solubility of an ionic compound – the smaller the value, the less soluble the compound in water. However, in using K_{sp} values to compare solubilities, it would choose compounds that have similar formulas, such AgCl and ZnS, or CaF_2 and $Fe(OH)_2$. There are two other quantities that express a substance's solubility: **molar solubility**, which is the number of moles of solute in 1 L of saturated solution (moles per liter), and **solubility**, which is the number of grams of solute in 1 L of saturated solution (grams per liter). Note that all these expressions refer to the concentration of saturated solutions at some given temperature (usually 25°C0. Figure 11 shows the relationships among solubility, molar solubility and K_{sp}.

Example 1. The solubility of calcium sulfate is found experimentally to be 0,67 g/L. Calculate the value of K_{sp} for this salt.

To convert solubility to K_{sp}, we need to convert g/L in mol/L. First, we calculate the numbers of moles of $CaSO_4$ dissolved in 1 L of solution:

$$\frac{0{,}67\ \text{g CaSO}_4}{1\ \text{L solution}} \times \frac{1\ \text{mol CaSO}_4}{136{,}2\ \text{g CaSO}_4} = 4{,}9 \times 10^{-7}\ \text{mol/L}.$$

The solubility equilibrium

$$CaSO_4\ (s) \leftrightarrow Ca^{2+}\ (aq) + SO_4^{2-}\ (aq)$$

shows that for every mole of $CaSO_4$ that dissolves, 1 mole of Ca^{2+} and 1 mole of SO_4^{2-} are produced. Thus, at equilibrium

$$[Ca^{2+}] = 4,9 \times 10^{-3}\ M \text{ and } [SO_4^{2-}] = 4,9 \times 10^{-3}\ M.$$

Now we can calculate K_{sp}:

$$K_{sp} = [Ca^{2+}] \cdot [SO_4^{2-}] = (4,9 \times 10^{-3}) \cdot (4,9 \times 10^{-3}) = 2,4 \times 10^{-5}.$$

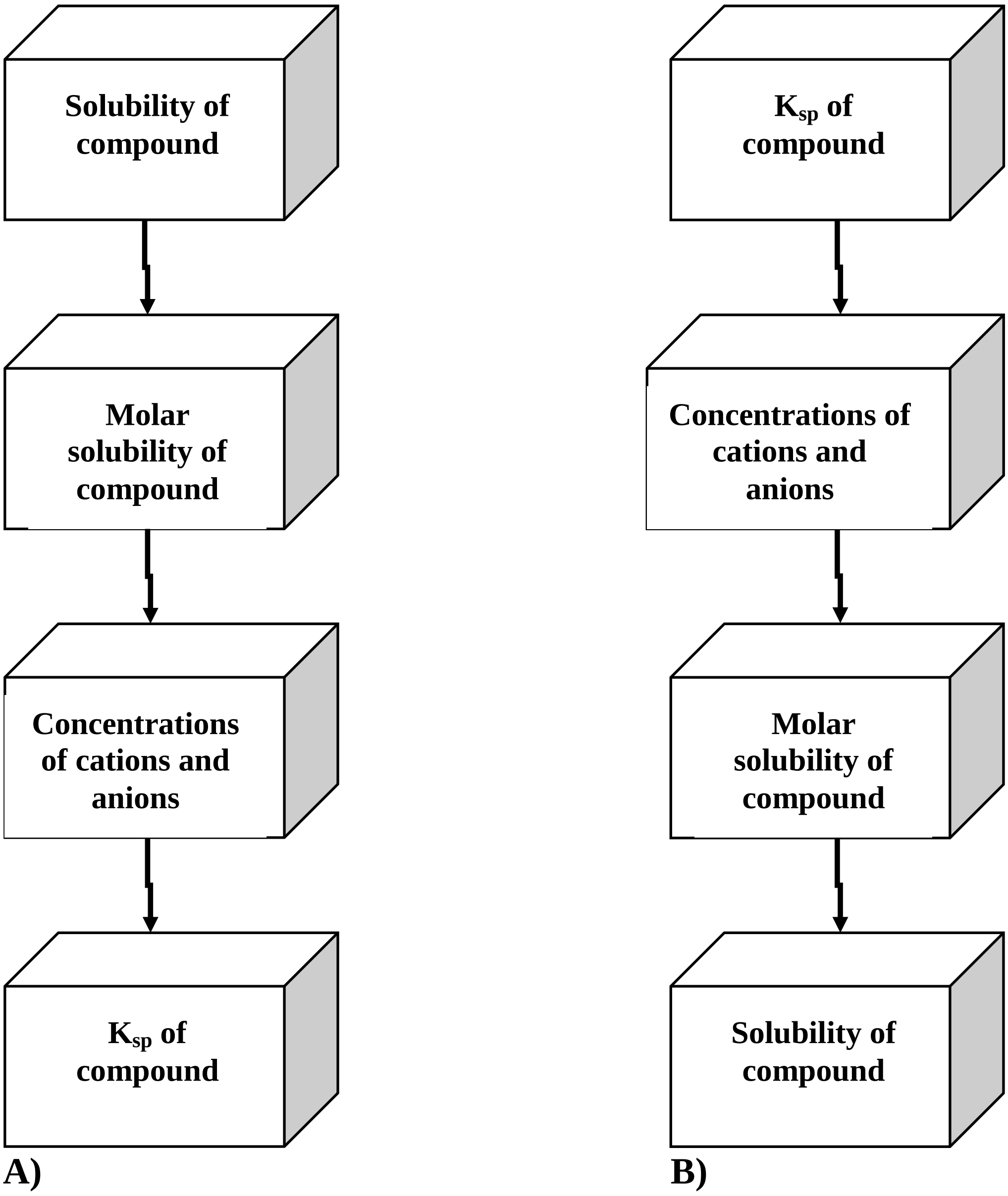


Figure 11 – Sequence of steps (A) for calculations K_{sp} from solubility data and (B) for calculating solubility from K_{sp} data

Example 2. Sometimes we are given the value of K_{sp} for a compound and asked to calculate the compound's molar solubility. For example, The K_{sp} of silver bromide AgBr is $7,7 \times 10^{-3}$. We can calculate its molar solubility by the same procedure as for acid ionization constants.

First we identify the species present at equilibrium. Here we have Ag^+ and Br^- ions. Let ***s*** be the molar solubility (in mol/L) of AgBr. Because one unit of AgBr yields one Ag^+ and one Br^- ion, at equilibrium both $[Ag^+]$ and $[Br^-]$ are equal to ***x***. We summarize the charges in concentrations as follows:

$$AgBr\ (s) \leftrightarrow Ag^+\ (aq) + Br^-\ (aq)$$

Initial (M):	0,00	0,00
Charge (M):	$+x$	$+x$
Equilibrium (M):	x	x

From Appendix 10 we write

$$K_{sp} = [Ag^+]\cdot[Br^-]$$
$$7{,}7\times10^{-3} = [x] \times [x]$$
$$x = \sqrt{7{,}7\times10^{-13}} = 8{,}8\times10^{-7}\ M$$

Therefore, at equilibrium

$[Ag^+]= 8{,}8\times10^{-7}M$

$[Br^-] = 8{,}8\times10^{-7}M$

Thus the molar solubility of AgBr also is $8{,}8\times10^{-7}M$. Knowing the molar solubility will enable us to calculate the solubility in g/L, as known in Example 1.

Example 3. Using the data of appendix 10, calculate solubility of copper(II) hydroxide $Cu(OH)_2$, in g/L. Determine value of pH, where precipitating of this compound will be start.

To convert K_{sp} to solubility, we need to calculate firstly the number of moles of the dissolved compound (that is, molar solubility) and then calculate the mass in grams using the molar mass of compound.

When $Cu(OH)_2$ dissociates, the species in solution are Cu^{2+} and OH^- ions. Let x the molar solubility of $Cu(OH)_2$. Because one unit of $Cu(OH)_2$ yields one Cu^{2+} ion and two OH^- ions, at equilibrium $[Cu^{2+}]$ is x and $[OH^-]$ is 2x. We summarize the charges in concentrations as follows:

$$Cu(OH)_2\ (s) \leftrightarrow Cu^{2+}\ (aq) + 2OH^-\ (aq)$$

Initial (M):	0,00	0,00
Charge (M):	$+x$	$+2x$
Equilibrium (M):	x	$2x$

$$K_{sp} = [Cu^{2+}]\cdot[OH^-]^2$$
$$2{,}2\times10^{-20} = [x] \times [2x]^2$$
$$x = \sqrt[3]{\frac{2{,}2\times10^{-20}}{4}} = 1{,}8\times10^{-7}\ mol/L.$$

Knowing that the molar mass of $Cu(OH)_2$ is 97,57 g/mol and knowing the molar solubility, we can calculate solubility in g/L, as:

Solubility of $Cu(OH)_2$ = $\frac{1{,}8\times10^{-7}\ \text{mol Cu(OH)}_2}{1\ \text{L soln}}\times\frac{97{,}57\ \text{g Cu(OH)}_2}{1\ \text{mol Cu(OH)}_2}=$

$= 1{,}8\times10^{-5}$ g/L.

Minimum concentration of OH^- for the start of precipitating is equal to:

$[OH^-] = 2x = 2\times1{,}8\times10^{-7}$ M $= 3{,}6\times10^{-7}$ M.

$pOH = -\lg [OH^-] = -\lg 3{,}6\times10^{-7} = -(-7)\times\lg 3{,}6 = 7\times0{,}556=3{,}89$.

$pH = 14 - pOH = 14 - 3{,}89 = 10{,}01$.

So, process of precipitation of $Cu(OH)_2$ starts on reaching pH=10,01 in solution.

4.3. Predicting precipitation reactions

It is possible to predict whether a precipitate will form when we mix solutions or add a soluble compound to a solution using knowledge of the solubility rules and the solubility products. This ability often has practical value in industrial and laboratory preparations; we can adjust the concentrations of ions until the ion product exceeds K_{sp} in order to obtain a given compound (in the form of a precipitate). The ability to predict precipitation reactions is also useful in medicine. For example, kidney stones, which can be extremely painful, consist largely of calcium oxalate CaC_2O_4 ($K_{sp} = 2{,}3\times10^{-9}$). The normal physiological concentration of calcium ions in blood plasma is about 5 mM (1mM = 1×10^{-3}M). Oxalate ions ($C_2O_4^{2-}$), derived from oxalic acid present in many vegetables such as rhubarb and spinach, react with calcium ions to form insoluble calcium oxalate, which can gradually build up in the kidneys. Proper adjustment of a patient's diet can help to reduce precipitate formation.

Example 4. Exactly 200 mL of 0,0040 M $BaCl_2$ are added to exactly 600 mL of 0,0080 M K_2SO_4. Will a precipitate form?

The ions present in solution are Ba^{2+}, Cl^-, K^+ and SO_4^{2-}. According to the solubility rules (table of salts solubility), the only precipitate that might form is $BaSO_4$:

$$Ba^{2+}\,(aq) + SO_4^{2-}\,(aq) \rightarrow BaSO_4\,(s)$$

The number of moles of Ba^{2+} present in the original 200 mL of solution is

$$200\ \text{mL}\times\frac{0{,}0040\ \text{mol Ba}^{2+}}{1\ \text{L soln}}\times\frac{1\ \text{L}}{1000\ \text{mL}}=8{,}0\times10^{-4}\ \text{mol Ba}^{2+}$$

The total volume after combining the two solutions is 800 mL. The concentration of Ba^{2+} in the 800 mL volume is

$$[Ba^{2+}] = \frac{8{,}0\times10^{-4}\,\mathrm{mol}}{800\,\mathrm{mL}}\times\frac{1000\,\mathrm{mL}}{1\,\mathrm{L\,soln}} = 1{,}0\times10^{-3}\,\mathrm{M}.$$

The number of moles of SO_4^{2-} in the original 600 mL solution

$$600\ \mathrm{mL}\times\frac{0{,}0080\,\mathrm{mol\,SO_4}^{2-}}{1\,\mathrm{L\,soln}}\times\frac{1\,\mathrm{L}}{1000\,\mathrm{mL}} = 4{,}8\times10^{-3}\ \mathrm{mol\ SO_4^{2-}}.$$

The concentration of SO_4^{2-} in the 800 mL of the combined solution is

$$[SO_4^{2-}] = \frac{4{,}8\times10^{-3}\,\mathrm{mol}}{800\,\mathrm{mL}}\times\frac{1000\,\mathrm{mL}}{1\,\mathrm{L\,soln}} = 6{,}0\times10^{-3}\,\mathrm{M}.$$

Now we must compare Q with K_{sp}. From Appendix 13, The K_{sp} for $BaSO_4$ is $1{,}1\times10^{-10}$.

As for Q,

$$Q = [Ba^{2+}]_0\cdot[SO_4^{2-}]_0 = (1{,}0\times10^{-3})\cdot(6{,}0\times10^{-3}0 = 6{,}0\times10^{-6}.$$

Therefore,

$$Q>K_{sp}.$$

The solution is supersaturated because the value of Q indicates that the concentrations of the ions are too large. Thus some of the $BaSO_4$ will precipitate out of solution until

$$[Ba^{2+}]\cdot[SO_4^{2-}]=1{,}1\times10^{-10}.$$

4.4. The common ion effect and solubility

As we have noted, the solubility product is equilibrium constant; precipitation of an ionic compound from solution occurs whenever the ion product exceeds K_{sp} for that substance. In a saturated solution of AgCl, for example, the ion product $[Ag^+]\cdot[Cl^-]$ is, of course, equal to K_{sp}. Furthermore, simple stoichiometry tells us that $[Ag^+] = [Cl^-]$. But this equality does not hold in all situations.

Suppose we study a solution containing two dissolved substances that share a common ion, say, AgCl and $AgNO_3$. In addition to the dissociation of AgCl, the following process also contributes to the total concentration of the common silver ions in solution:

$$AgNO_3\,(s) \xrightarrow{H2O} Ag^+\,(aq) + NO_3(aq).$$

If $AgNO_3$ is added to a saturated AgCl solution, the increase in $[Ag^+]$ will make the ion product greater than the solubility predict:

$$Q = [Ag^+]_0\cdot[Cl^-]_0>K_{sp}.$$

To reestablish equilibrium, some AgCl will precipitate out the solution, as Le Chátelier's principle would predict is once again equal to K_{sp}. The effect of adding a common ion, then, is a *decrease* in the solubility of the salt (AgCl) in solution. Note that in this case $[Ag^+]$ is no longer equal to $[Cl^-]$ at equilibrium: rather, $[Ag^+]>[Cl^-]$.

Example 5. Calculate the solubility of silver chloride (in g/L) in a $6{,}5\times10^{-3}$ M silver nitrate solution.

This is a common ion effect problem. Note that the presence of the common ion (Ag^+) does not affect the value of K_{sp} of AgCl. We proceed as follows.

The relevant species in solution are Ag^+ ions (from both AgCl and $AgNO_3$) and Cl^- ions. The NO_3^- ions are spectator ions.

Because $AgNO_3$ is a soluble strong electrolyte, is dissociates completely:

$$AgNO_3\,(s) \xrightarrow{H2O} \underset{6{,}5\times10^{-3}\ M}{Ag^+\,(aq)} \quad + \quad \underset{6{,}5\times10^{-3}\ M}{NO_3(aq).}$$

Let x be the molar solubility of AgCl in $AgNO_3$ solution. We summarize the charges in concentrations as follows:

$$AgCl\,(s) \leftrightarrow \quad Ag^+\,(aq) \quad + \quad Cl^-\,(aq)$$

Initial (M):	$6{,}5\times10^{-3}$ M	0,00
Charge (M):	$+\,x$	$+\,x$
Equilibrium (M):	$6{,}5\times10^{-3}+x$	x

$$K_{sp} = [Ag^+]\cdot[Cl^-]$$

$$1{,}6\times10^{-10} = \boldsymbol{(6{,}5\times10^{-3}+x)\cdot(x)}$$

Because AgCl is quite insoluble and the presence of Ag^+ ions from $AgNO_3$ further lowers the solubility of AgCl, $\boldsymbol{x}$ must be very small compared with $6{,}5\times10^{-3}$. Therefore, applying the approximation $(6{,}5\times10^{-3}+\boldsymbol{x})\approx6{,}5\times10^{-3}$, we obtain

$$1{,}6\times10^{-10} = 6{,}5\times10^{-3}\cdot \boldsymbol{x}$$

$$\boldsymbol{x} = 2{,}5\times10^{-8}\ M.$$

At equilibrium

$$[Ag^+] = (6{,}5\times10^{-3} + 2{,}5\times10^{-8})\ M \approx 6{,}5\times10^{-3}\ M$$

$$[Cl^-] = 2{,}5\times10^{-8}\ M$$

And so our approximation was justified in the previous step. Because all the Cl^- ions must come from AgCl, the amount of AgCl dissolved in $AgNO_3$? Solution also is $2{,}5\times10^{-8}$ M. Then, knowing the molar mass of AgCl (143,4 g), we can calculate the solubility of AgCl as:

Solubility of AgCl in $AgNO_3$ solution =

$$= \frac{2{,}5\times10^{-8}\ \text{mol AgCl}}{1\ \text{L soln}} \times \frac{143{,}4\ \text{g AgCl}}{1\ \text{mol AgCl}} = 3{,}6\times10^{-6}\ \text{g/L.}$$

Example 6. Calculate the solubility of calcium phosphate (in g/L) in a pure water and in 1×10^{-3} M sodium phosphate solution (K_{sp} ($Ca_3(PO_4)_2$)= 3×10^{-33}).

This is a common ion effect problem. Note that the presence of the common ion (PO_4^{3-}) does not affect the value of K_{sp} of $Ca_3(PO_4)_2$. We proceed as follows.

The relevant species in solution are Ca^{2+} ions (from both $Ca_3(PO_4)_2$ and Na_3PO_4) and PO_4^{3-} ions (from both $Ca_3(PO_4)_2$ and Na_3PO_4). The Na^+ ions are spectator ions.

Because Na_3PO_4 is a soluble strong electrolyte, is dissociates completely:

$$\begin{array}{lccc} Na_3PO_4\ (s) \xrightarrow{H2O} & 3\ Na^+\ (aq) & + & PO_4^{3-}\ (aq). \\ & 3\times10^{-3}\ M & & 1\times10^{-3}\ M \end{array}$$

Let x be the molar solubility of $Ca_3(PO_4)_2$ in Na_3PO_4 solution. We summarize the charges in concentrations as follows:

$$Ca_3(PO_4)_2\ (s) \leftrightarrow\ 3\ Ca^{2+}\ (aq)\ +\ 2\ PO_4^{3-}\ (aq)$$

Initial (M):	0,00	1×10^{-3} M
Charge (M):	$\boldsymbol{+3x}$	$\boldsymbol{+2x}$
Equilibrium (M):	$+\boldsymbol{3x}$	1×10^{-3} M $\boldsymbol{+2x}$

$$K_{sp} = [Ca^{2+}]^3\cdot[PO_4^{3-}]^2$$

$$3\times10^{-33} = (3x)^3\cdot(1\times10^{-3}\ M + 2x)^2$$

Because $Ca_3(PO_4)_2$ is quite insoluble and the presence of PO_4^{3-} ions from Na_3PO_4 further lowers the solubility of $Ca_3(PO_4)_2$, $\boldsymbol{x}$ must be very small compared with 1×10^{-3}. Therefore, applying the approximation $(1\times10^{-3}\ M + 2x)^2 \approx 1\times10^{-6}$, we obtain

$$x = \sqrt[3]{\frac{3\times10^{-33}}{27\times1\times10^{-6}}} = 0{,}48\times10^{-9}\,M.$$

Then, knowing the molar mass of $Ca_3(PO_4)_2$ (310,0 g), we can calculate the solubility of $Ca_3(PO_4)_2$ as:

Solubility of $Ca_3(PO_4)_2$ in Na_3PO_4 solution

$$= \frac{0{,}48\times10^{-9}\ \text{mol}\ Ca_3(PO_4)_2}{1\,\text{L soln}} \times \frac{310{,}0\ \text{g}\ Ca_3(PO_4)_2}{1\,\text{mol}\ Ca_3(PO_4)_2} = 1{,}5\times10^{-7}\ \text{g/L}.$$

4.5. Gravimetry

Gravimetric analysis, the most “classical” of all quantitative methods (among the oldest of analytical techniques), relays on some final determination of weight. The compound of interest (analyte) is precipitated in a solid compound of known composition. The mass of the analyte present in the sample is determined from the mass of the precipitate.

Since weight can be measured with greater accuracy than any other fundamental property, gravimetric analysis was (**it is** yet) one of the most accurate analytical methods. Gravimetric procedures are lengthy and tedious compared against instrumental methods; and, in addition, samples may have to be extensively treated to remove interfering substances. As a result, only a very few gravimetric methods are currently used in environmental analysis (see Table 9).

Based on the preparation of the sample before weighing the analyte compound, there are four fundamental types of gravimetric analysis:

1. Physical gravimetry, is the most common type used in environmental control engineering. It involves the physical separation and classification of matter based on volatility and particle size (e.g., total suspended solids).

2.Thermogravimetry, for the analysis of volatile solids. Changes in the sample mass when heated are recorded.

3. Electrogravimetry or electro-deposition which usually involves the electrochemical reduction and simultaneous deposition of metal ions at a cathode.

4.Chemical precipitation, the most common in a “classical” sense. It relies on a chemical reaction to transform the solved analyte in a very low soluble precipitate. Its most important application in the environmental field is with the analysis of sulfate or sulfite.

These differ in the preparation of the sample before weighing of the analyte. Physical gravimetry is the most common type used in agricultural analysis. It involves the physical separation and classification of matter in environmental samples based on volatility and particle size (e.g., total suspended solids). With thermogravimetry, samples are heated and changes in sample mass are recorded. Volatile solids analysis is an important example of this type of gravimetric analysis. As the name implies, precipitative gravimetry relies on the chemical precipitation of an analyte. involves the electrochemical reduction of metal ions at a cathode, and simultaneous deposition of the ions on the cathode.

Table 9. Gravimetric methods in environmental analysis control

Type of gravimetry	**Analyte**	**Procedure**
1	**2**	**3**
Physical	Total Solids	Evaporation
	Suspended Solids	Filtration
	Dissolved Solids	Filtration + Evaporation

1	2	3
Physical	Oil & Grease	Extraction with $C_2Cl_3F_3$ + distillation of solvent
	Surfactants	Extraction into ethylacetate + evaporation
	Volatile Solids	Evaporation + 550°C for 15 min
Thermal	Volatile Solids	Evaporation + 550°C for 15 min
	Volatile Suspended Solids	Filtration + 550°C for 15 min
Precipitative	Mg^{2+}	With Diammonium hydrogen phosphate and final pyrolysis
	Na^{+}	With zinc uranyl acetate
	Silica	Precipitation/ ignition/ volatilization (with HF)
	SO_4^{2-}	With Ba^{2+}

4.5.1. Physical Gravimetry

As the operational definition of Total Solids (TS) content has been adopted through years of use the following "all matter that remains as residue upon evaporation and drying at 180 °C for one hour". This is **an operational definition** because solids in a water or wastewater sample are a diverse collection of dissolved and particulate matter rather a specific chemical compound. According to this operational definition and depending on certain empirical parameters the result may be smaller or greater than the amount of solids present in the sample.

An operational criteria serves for a classification of total solids; this definition establishes the following: all solids passing through a filter paper of a certain pore size (e.g., 1.5 microns) are the total dissolved solids (TDS) and those retained on the filter are the total suspended solids (TSS). Some authors prefer to define the total dissolved solids as all matter that is not retained by a filter, and then, it is not lost by evaporation and drying at 180°C for one hour.

Most of the impurities in ***potable waters*** are inorganic salts that resulted in the dissolved state. Thus, the parameters TS (total solids) and TDS (total dissolved solids) have a relevant importance. Sources of drinking water containing high concentrations of inorganic salts are not suitable (more than 1000 mg/L TDS are unacceptable), because such materials are often difficult to remove in the treatment-plants. Waters of this type are even unsuitable for agricultural uses due to the negative effect on plants of the high ionic concentrations.

In natural water samples, the TDS (total dissolved solids) usually correlates well with the total hardness (expressed as total [Ca] + [Mg]); which results as an useful parameter to assess either the need for “softening” and the corrosivity of a water.

It is very important to avoid unrepresentative sampling or particle break-up, this should be considered either at the point of sampling and at laboratory sub-sampling. The former topic means not disturbing the flow pattern of the sample stream or at least, the disturbance should be minimized.

When the presence of settle able solids is suspected and for producing a homogeneous cross-section of settle able solids, the mixing at the point of sampling is sufficient and depth-integrated sampling is not required.

PROCEDURE

1. Clean and dry three porcelain crucibles (see note below). Make sure crucibles are marked so they can be distinguished from one another.
2. Dry crucibles in the oven at 100-110°C for one hour or overnight. The crucibles should be put in a labeled beaker and covered with a watch glass when in the oven.
3. Cool the crucibles in a desiccator (Fig. 12) for 20 minutes and weigh.

Figure 12 - Desiccator

4. Repeat step 2 and 3, this time drying for only 20 minutes.
5. Repeat this procedure until the mass of each crucible agrees to within 0.3 mg.

Note: Cleaning Procedure for Porcelain Crucibles

If there is a gray or white residue in the crucible, add a few drops of conc. NH_3 (aq) and apply vacuum to pull the resulting solution through the fritted bottom. Follow by rinsing with copious quantities of H_2O. Make sure you have about 100 mL of H_2O in the filter flask to dilute the acid when it comes through. If a dark stain remains, empty the contents of the filter flask and add a few mL of conc. HNO_3 to the crucible. Apply vacuum as before, and after the solution goes through, empty the flask and rinse the crucible. If there is a reddish stain in the crucible, a few drops of conc. HCl should remove it nicely. Proceed as with HNO_3 above. If crucible does not filter rapidly after cleaning see the TA.

Waste Note: The NH_3 (a base) waste is separate from the HNO_3 and HCl (acids) waste.

Worked Examples

1. A certain barium halide exists as the hydrated salt $BaX_2 \cdot 2H_2O$, where X is the halogen. The barium content of the salt can be determined by gravimetric method. A sample of the halide (0.2650 g) was dissolved in water (200 cm^3) and excess sulfate acid added. The mixture was then heated and held at boiling for 45 minutes. The precipitate (barium sulfate) was filtered off, washed and dried. Mass of precipitate obtained = 0,2533 g. Determine the identity of X.

Answer:

The precipitate is barium sulfate. The first stage is to determine the number of moles of barium sulfate produced, this will, in turn give us the number of moles of barium in the original sample.

Molar Mass of barium sulfate: M ($BaSO_4$) = 137,34 (Ba) + 32,06 (S) + (4x16,00)(4 x O) = 233,40 g/mol;

Number of moles υ: $\upsilon = \frac{m}{M(BaSO_4)}$ = 0,2533 / 233,40 = $1{,}09 \cdot 10^{-3}$.

This is the number of moles of barium present in the precipitate and, therefore, the number of moles of barium in the original sample. Given the formula of the halide, (i.e. it contains one barium per formula unit), this must also be the number of moles of the halide. From this information we can deduce the relative molecular mass of the original halide salt:

$$M_r \text{ (halide salt)} = m/\upsilon = 0.2650/1{,}09 \cdot 10^{-3} = 244{,}18 \text{ g/mol}.$$

The relative atomic mass of 2X will be given by the M_r of the whole salt - that of the remaining components; So, relative atomic mass of 2 X = 244,18 – 173,37 = 70,81.

$$2\ X = 70{,}81, \text{ so } X = 35{,}41 \text{ g/mol}.$$

The M_r of chlorine is 35,45 which is in good agreement with the result obtained and hence the halide salt is hydrated barium chloride and X = Chlorine.

4.5.2. Laboratory work - Physical gravimetry. Determination of water in Hydrated Barium Chloride

Determination of water in Hydrated Barium Chloride:

Determine how much water there is in hydrated barium chloride.
Also solve n in $BaCl_2$ + n H_2O.
Chemicals and apparatus:
Porcelain crucible and lid;
Pipe-clay triangle;
Desiccator;
Tongs;
AR (analytical range) hydrated barium chloride.
Lab:

First, it is necessary to clean the crucible and lid that we are going to use to get a more exact answered, so we heat the crucible and lit for about ten minutes. Then we let it cool for one minute so we can put it in the desiccator to cool to room temperature. We then weigh the empty crucible and lid *(w1),* they were measured to 16,98 grams. Then we add AR hydrated barium chloride and measure the weight again *(w2)* to 19,22 grams, that is 2,24 grams barium chloride and 16,98 grams crucible. We then heat everything for about 15 minutes and the reweight *(w3)* everything to 18,88 grams. That is, the water that was vaporized weighted 0,34 grams.

Conclusion: Mass of anhydrated barium chloride:
(w3 - w1)=1,9 grams.
Mass of water removed: (w2 - w3) = 0,34 grams.
Moles of $BaCl_2$: $\upsilon = 0.009$;
Moles of H_2O: $\upsilon = 0{,}0189$.
N (numbers of water moles) = $\upsilon\ (H_2O)/\ \upsilon\ (BaCl_2)$ =
$0{,}0189/0{,}009=2{,}099 \approx 2$.
Formula of salt: $BaCl_2{\cdot}2H_2O$.

4.5.3. Precipitative Gravimetry

For successful determinations the following criteria must be met: the desired substance must be completely precipitated. In most determinations the precipitate is of such low solubility that losses from dissolution are negligible. An additional factor is the "common ion" effect, this further reduces the solubility of the precipitate. When Cl^- is precipitated out by addition of Ag^+

$$Ag^+ + Cl^- \rightarrow AgCl\ (s)$$

The low solubility of AgCl is reduced still further by the excess of Ag^+, which is added, pushing the equilibrium to the right. It can further decrease the solubility by decreasing the temperature of the solution by using an ice bath. The weighed form of the product should be of known composition. The product should be "pure" and easily filtered. It is usually difficult to obtain a product, which is "pure", i.e. one which is free from impurities but careful precipitation and sufficient washing helps reduce the level of impurity.

Mechanism of Precipitation

After the addition of the precipitating agent to the solution of the ion under analysis there is an initial **induction period** before nucleation occurs. This induction period may range from a very short time period to one which is relatively long, ranging from almost instantaneous to several minutes.

After induction, **nucleation** (Fig. 13) occurs, here small aggregates or nuclei of atoms form and it is from these "clumps" of atoms that the crystals, which form the filtrate, will grow. These nuclei may be composed of just a few atoms each so there may be up to 10^{10} of the nuclei per mole of precipitating product. As these nuclei form ions from the solution (which at this point are in excess) congregate around them. For example if hydrochloric acid was added very slowly to a solution of silver nitrate, silver chloride nuclei would form and silver ions (which would be in excess relative to Cl^- ions) would congregate around them.

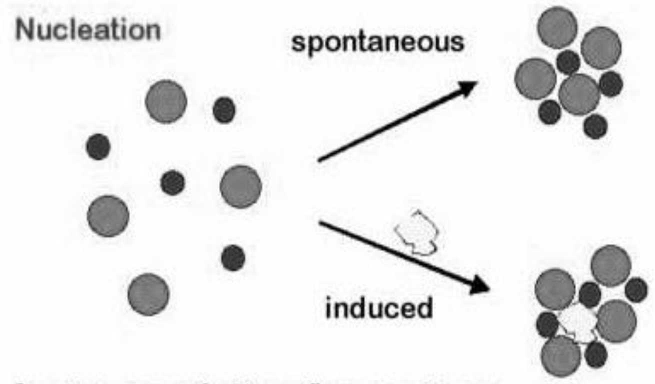


Figure 13 – Mechanizm of nucleation

In addition to the **primary adsorbed silver ion**, there are some nitrate ions aggregating further from the AgCl nucleus. These are counter ions and tend to aggregate around the $[AgCl:Ag]^+$ centre because these centres have a net positive charge (excess Ag^+) and additional negative charge is required to maintain electrical neutrality. The counter ions are less tightly held than the primary adsorbed ions and the counter ion layer is somewhat diffuse and contains ions other than those of the counter ions. These layers of charges are known as the **electric double layer** (Fig. 14).

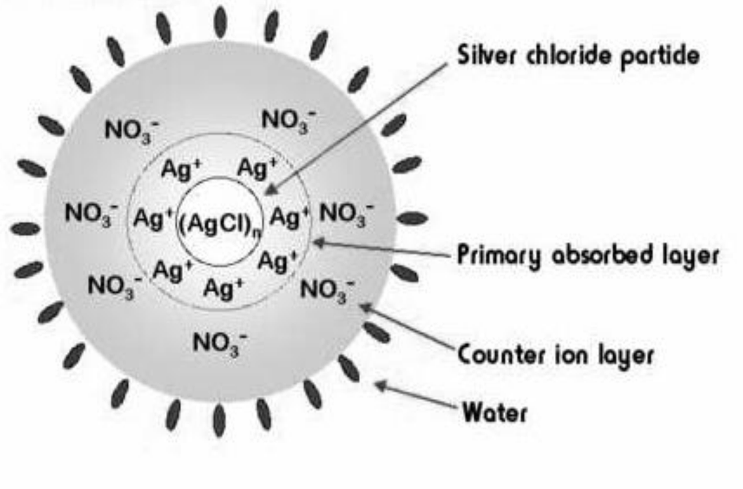


Figure 14 – Structure of Silver Chloride colloidal particle

After nucleation growth occurs, large nuclei grow at the expense of smaller nuclei, which dissolve. This process helps produce more easily filtered crystals (since it produces larger crystals).

Growth of larger nuclei or crystallites can be encouraged by **digestion,** a process that involves heating the solid and mother liquor for a certain period of time. During digestion, small particles dissolve and larger ones grow. Digestion of the product is an important practical process and you will find that most if not all gravimetric analysis involves a digestion period.

Conditions for analytical precipitation

In an ideal world, an analytical precipitate for gravimetric analysis should consist of perfect crystals large enough to be easily washed and filtered. The perfect crystal would be free from impurities and be large enough so that it presented a minimum surface area onto which foreign ions could be adsorbed. The precipitate should also be "insoluble" (i.e. be of such slight solubility that loses from dissolution would be minimal).

Without going into detail, it has been shown (Von Weimarn) that the particle size of precipitates is inversely proportional to the relative super-saturation of the solution during precipitation;

$$\text{Relative super-saturation} = (Q-S)/S$$

For the best possible results, conditions need to be adjusted such that Q will be as low as possible and S will be relatively large. The following methods are used to approach these criteria:

Precipitation from hot solution. The solubility S of precipitates increases with temperature and so an increase in S decreases the supersaturation.

Precipitation from dilute solution. This keeps Q low. Slow addition of precipitating reagent with effective stirring. This also keeps Q low; stirring prevents local high concentrations of the precipitating agent.

Precipitation at a pH near the acidic end of the pH range in which the precipitate is quantitative. Many precipitates are more soluble at the lower (more acidic) pH values and so the rate of precipitation is slower.

Co-precipitation

Co-precipitation occurs to some degree in every gravimetric analysis (especially Barium Sulphate and those involving hydrous oxides).

Surface adsorption

Here unwanted material is adsorbed onto the surface of the precipitate. Digestion of a precipitate reduces the amount of surface area and hence the area available for surface adsorption. Washing can also remove surface material.

Occlusion

This is a type of co-precipitation in which impurities are trapped within the growing crystal (Fig. 15).

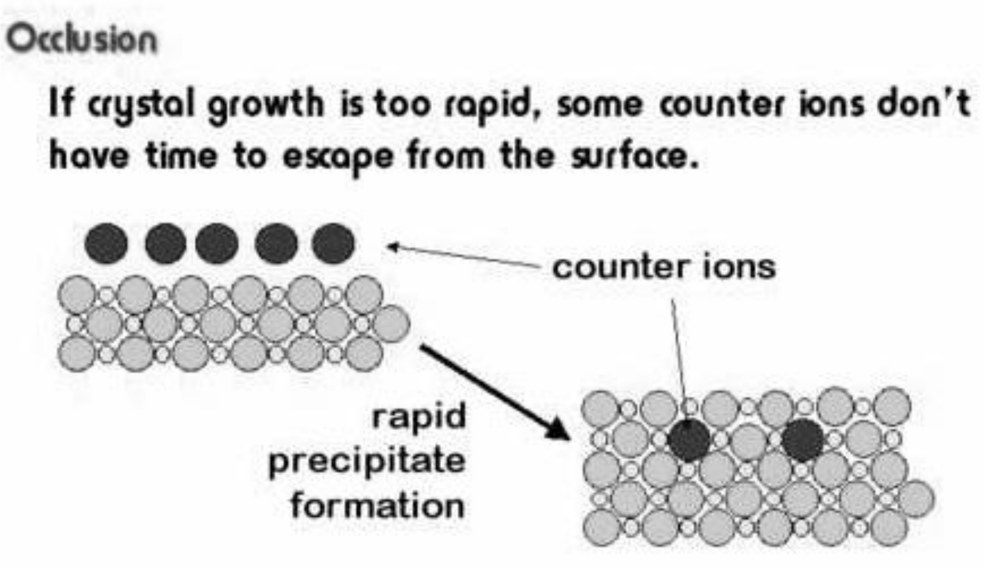


Figure 15 – Mechanizm of occlusion

Post-precipitation

Sometimes a precipitate standing in contact with the mother liquor becomes contaminated by the precipitation of an impurity on top of the desired precipitate.

Calculations

You may find reference to the gravimetric factor f in some texts - this is the ratio of relative molar mass (M_r) of substance sought to that of substance weighed:

$$f = \frac{M_r \text{ (substance sought)}}{M_r \text{ (substance weighed)}}. \qquad (8)$$

4.5.4. Laboratory work - Precipitate gravimetry. Determination of Sulfates content in water or Barium content in Hydrated Barium Chloride

Sulfate content

Method based on the weight of precipitated $BaSO_4$.

The historical method of choice for sulfate in waters and wastewaters is the gravimetry with barium:

$$Ba^{+2} + SO_4^{-2} = BaSO_4 \text{ (precipitated)}$$

1. Barium sulfate precipitates quantitatively by adding excess of ion Ba^{2+} under acidic conditions ($5x10^{-2}$ mol L^{-1} in hydrochloric acid),

Low pH is required to avoid the co-precipitation of barium carbonates and/or phosphates.

2. The formation of high purity and non-filterable crystals implies to allow reaction to continue for at least 2 hours at temperature over 80- 90°C. This process (digestion of the precipitate) minimizes the formation of filterable $BaSO_4$ crystals from the initial colloidal particles.

3. Filter the precipitate by decantation on a filter paper and the resulting solid mass is washed and dried in an oven for 1 hour at 800°C.

During this process the reducing character of the filter paper can originate barium sulfur,

$$BaSO_4 + C \rightarrow BaS + 4\ CO.$$

To avoid it, add a drop of sulfuric acid and repeat the calcination.

This calcination procedure (1 hour at 800–900ºC) should be performed on the porcelain crucible used for this operation.

4. Finally it is weighed at room temperature (keep it into a desiccator). Final weight, total minus tare (crucible).

Determination of barium as $BaSO_4$. The precipitation is not carried out by slow addition of precipitant to the analyte containing solution. Such a procedure tends to produce conditions of super-saturation and a consequent rapid formation of small, relatively impure solid particles results. This effect cannot be entirely eliminated and is a source of error. The homogeneous precipitation techniques are able to avoid this erroneous effect; the precipitating reagent is generated slowly and homogeneously in presence of hydrochloric acid in boiling aqueous solution.

Procedure:

1. Calculations:

|Mass of examined example.

Remember, that recommended mass of crystalline precipitate (according Tananaev's data) is near 0,5 g.

So, 1 mol of $BaSO_4$ (233,43 g) precipitates from 1 mol $BaCl_2 \cdot 2H_2O$ (244,31 g);

0,5 g of $BaSO_4$ precipitates from x g of $BaCl_2 \cdot 2H_2O$;

x = m (examined solid salt) = $\frac{0{,}5\,\text{g} \times 244{,}31\,\text{g/mol BaCl}_2 \cdot 2\text{H}_2\text{O}}{233{,}43\,\text{g/mol BaSO}_4} = 0{,}52\,\text{g}.$

Volume of precipitate agent 2 N H_2SO_4.

According to reaction of presipitation,

1 mol $BaCl_2 \cdot 2H_2O$ (244,31 g) reacts with 1 mol H_2SO_4 (98,00 g);

0,52 g $BaCl_2 \cdot 2H_2O$ reacts with y g H_2SO_4.

y = m (H_2SO_4) = $\frac{0{,}52\,\text{g} \times 98{,}00\,\text{g/mol H}_2\text{SO}_4}{244{,}31\,\text{g/mol BaCl}_2 \cdot 2\text{H}_2\text{O}} = 0{,}2086\,\text{g}.$

1000 mL of 2 N H_2SO_4 contains $2 \cdot 49$ g = 98 g solyte;

z mL of 2 N H_2SO_4 contains 0,2086 g of solyte.

z = V (2 N H_2SO_4) = $\frac{1000\,\text{mL} \times 0{,}2086\,\text{g}}{98\,\text{g}} = 2{,}13\,\text{mL}.$

Taking into account 1,5-2 divisible excess of precipitate agent, it is nessecary to use 3,2 – 4,2 mL of 2 N H_2SO_4.

2. Determine mass of examined salt, using analytical balance.

Note W_1 = 0,xxx g (your result).

3. Weigh empty clean calcinated during 30 min. porcelain crucible **(remember number of crucible!)**

Note $W_{crucible}$ = 0,yyy g (your result).

4.Weigthed mass of salt transport quantitively to the 350-300 mL beaker, washing off solid by hor DW. Total volume of water in beaker must be not more 100-150 mL. Add 3 mL of 2N HCl for acidifation of solution.

5. Prepare solution of precipitate agent in the other 100-150 mL beaker, added 4 mL of 2 N H_2SO_4 and 25-50 mL of hot DW and stir up mixture.

6. Solutions of $BaCl_2$ and H_2SO_4 warm up practically to boiling state (to 80^0C). Very slowly, add by drops solution of H_2SO_4 to solution of Barium salt, stirring well permanently.

7. Let beaker with mixture settle for 24 hours at room temperature and protected from dust by paper list, note surname of student.

8. Filter on paper (no ashes material) and wash with a lot of boiling water up to no sulphate anions can be detected in the filtrate. If your filtrate remains clear, dispose of the filtrate in the appropriate waste container.

9. Dry filter with precipitate at 110ºC during 0,5-1 hour.

10. Ash filter with precipitate by heating in gas burner.

11. Then calcinate the precipitate with the aid of porcelain crucible in muffle at $800\text{-}900^0C$ duting 30-35 minutes.

12. Cool crucible to room temperature into a desiccator.

13. Weigh cruciblewith calcinated precipitate.
Note W_2 = 0,zzz g (your result).

14. Calculate content of barium in examined example of Barium chloride:

1 mol (233,43 g) $BaSO_4$ contains 1 mol (137,34 g) of Ba;
m ($BaSO_4$) = $W_2 - W_{crucible}$ contains x g of Ba.
So,

$$x=m(Ba)=\frac{m\,(BaSO_4)\cdot 137{,}34\,g}{233{,}43\,g}=0{,}5884\,m(BaSO_4)=0{,}5884\,(W_2-W_{crucible})$$

Calculated mass of Ba contains in initial mass of examined mass of Barium Chloride (W_1).

So,
W_1 g of Barium Chloride is 100% by mass;
m(Ba) g of Barium is z % by mass.

$$z=\%Ba=\frac{0{,}5884(W_2-W_{crucible})\times 100\%}{W_1}=ZZ{,}ZZ\ \%.$$

Determined figure control with lector.

Calculate absolute and relative errors of analysis:

Absolute error:

Δ = |%Ba experimental (your result) - %Ba true (noted by teacher)|.

Relative error:

$$\sigma = \frac{\Delta}{\%\text{Ba true}} \times 100\%.$$

Remamber, that relative error of gravimetry is not more 2%.

PROBLEMS

1. When a sample of impure potassium chloride (0,4500 g) was dissolved in water and treated with an excess of silver nitrate, 0,8402 g of silver chloride was precipitated. Calculate the percentage KCl in the original sample. (Answer: 97,12 %).

2. The phosphate in a 1,000 g fertilizer was precipitated as magnesium ammonium phosphate, $MgNH_4PO_4$. Ignition at 900°C converted the precipitate to magnesium diphosphates, $Mg_2P_2O_7$, which weighed 0,2550 g. Calculate the percentage of phosphorus in the fertilizer.

3. An organic insecticide was decomposed by an oxygen combustion procedure to convert the chlorine in the molecule to water-soluble chloride. The chloride was precipitated as silver chloride. 0,7715 g precipitate of silver chloride was obtained from a 0,5000g sample of insecticide. Calculate the percentage of chlorine in the insecticide.

4.6. Fundamentals of Titrimetry

Vocabulary

English	Українська назва	English	Українська назва
Titration	Титрування	Primary standard	Первинний стандарт (вихідна речовина)
Equivalence point	Точка еквівалентності	Secondary standard	Вторинний стандарт (робоча речовина, робочий розчин)
Direct titration	Пряме титрування	Equimolar amounts	Еквімолярні кількості
Back titration	Обернене титрування	Working solutions	Робочі розчини
Internal indicator	Зовнішній індикатор	Borax	Бура
External indicator	Внутрішній індикатор	Acid-base indicator	Кислотно-основний індикатор
Endpoint	Кінцева точка титрування	Metal-chromic indicator	Металохромний індикатор

Volumetric or titrimetric analysis is a classic quantitative method which employs an exactly measured volume of a standard solution containing a known concentration of reagent "A"; this reagent A is added step by step (from a burette) to the unknown concentration of the analyte “B” in the sample; the process proceeds until a perceptible change is produced (chemical indicator). The change, “end-point”, should be produced as close as possible to the complete reaction A + B in an “stoichiometric completion”. This theoretical point is known as the “equivalence-point”; where the number of added A equivalents to the sample solution equals the number of equivalents of "B" originally present.

Alternatively, a non-perceptible change could be also used, a “physical indicators” in which a physical property (conductivity, absorbance, etc.) is continuously measured. If the A additions to the sample proceeds far away from the equivalence point; further calculations allow to obtain the endpoint.

Two basic modalities are normally used: namely, direct titration (as above reported) and back titration. The latter is based on the addition of an intermediate reagent having the excess (not reacted with the analyte) is titrated.

Titrimetric methods reach a precision of up to 0.1%. Accuracy is related to the coincidence among end-point (or indicator point) and the equivalence-point.

Several basic requirements can be reported for a well-defined titrimetry:

1. A quick and quantitative reaction A + B is necessary.
2. A standard titrant solution of accurately known concentration of A to react with the analyte with a well-known and repeatable stoichiometric procedure.
3. An indicator (external or internal) to identify the endpoint. The random and systematic error resulting from the empirical estimation of the endpoint may be estimated by conducting a blank titration.
4. When the chemical for the titrant solution is not available in a kinetically stable form of pure and well-defined composition, the titrant must be standardized. This operation is an independent titration against stable, pure chemical known as a primary standard.
5. Accurate measurements of the sample and added titrant volumes.
6. It should be interesting if possible to have an A + B reaction sufficiently selective to avoid a previous sample treatment to remove interferences.

Titrations can be performed ***manually*** step by step (or point by point), or ***automatically***, where the titrant A is introduced continuously. At present, in analytical chemistry automation is of paramount importance for the following reasons:

1. convenience and speed,
2. performing analysis without supervision,
3. anable application of elaborate techniques for analyzing the data by computerized systems.

For automatic transfer of the titrant to the analyte solution are proposed several instrumental devices:

1. ***Piston burettes*** are highly reliable and do not require calibration,
2. ***Peristaltic pumps*** highly versatile and reliable. However and due to the changing properties of the flexible tubing they need to be periodically calibrated.
3. ***Suction-stroke piston pumps or metering pumps*** are more precise and require less calibration; they enjoy a similar degree of versatility.

Other empirical limitation of the pumps is the use of corrosive reagents, highly concentrated mineral acids (not in titrimetry) and organic solvents. There are commercially available acid and solvent resistant tubing.

Several advantages of these pumps are the simplicity of operation, simple and reliable control of flow-rate, easily automated, allow to work in a wide range of flow rates (for the titrant transfer; a relevant parameter to be optimized). For titrations in small volumes low flow rates are used (0.1 - 1 mL/min).

There are very relevant factors as stirring speed, configuration of the cell, input of titration, etc. Kinetics of the volumetric reaction and the response of the indicator system are of paramount importance (table 10).

Table 10 - Titrimetric methods for environmental water analysis

Analyte (A)	Standard-ized titrant solution (B)	Chemical Indicator (internal) Observed change	Sample pre-treatment	Volumetric reaction
1	2	3	4	5
Neutralization (acid-base)				
Alkalinity	HCl	-	-	$OH^- + H^+$
Acidity	NaOH	-	-	$H^+ + OH^-$
Nitrogen (III)	H_2SO_4	Methyl red	Digest/disti-llation nh_3	Macro-Kjeldahl & acidimetric
Volatile Acids	NaOH	Phenolphthalein	Distillation	Distillation
Precipitation				
Chloride	$AgNO_3$	Potassium chromate yellow-precipitate	-	$Ag^+ + Cl^- = AgCl\downarrow$
Chloride	Hg^{2+} nitrate	Diphenyl-carbazone	-	$Hg^{2+} + 2Cl^- = HgCl_2\downarrow$
Complex formation				
Ca^{2+}	EDTA	Eriochrome Blue Black R intense red - deep blue	pH 12	$Ca\text{-}EDTA^{2-}$ Direct titration
Hardness	EDTA	Eriochrome Black T intense red - deep blue	pH 10	As Ca and Mg total amounts, expressed as carbonates

1	2	3	4	5
Oxidation/Reduction				
Dissolved O_2(DO)	$Na_2S_2O_3$	Starch Deep blue – colorless (white turbidity)	Mn^{2+}, I(I^-)	Winkler
Ca^{2+}	$KMnO_4$	auto	oxalate	Permanganate
Chlorine/ClO_2	$Na_2S_2O_3$	Starch Deep blue – colorless (white turbidity)	I(I^-)	I_3^- - $S_2O_3^{2-}$
SO_3^{2-}	$Na_2S_2O_3$	Starch Deep blue – colorless (white turbidity)	I(I^-)	I_3^- - $S_2O_3^{2-}$
Chlorine/ClO_2	$FeSO_4$	DPD	-	DPD Ferrous
Concentration of dissolved oxygen, COD	$Fe(NH_4)_2(SO_4)_2$	Ferroin	$K_2Cr_2O_7$	-

Volumetric or titrimetric analyses are quantitative analytical techniques, which employ a titration in comparing an unknown with a standard.

The process of obtaining quantitative information of a sample using a fast chemical reaction by reacting with a certain volume of reactant whose concentration is known is called **titration**.

In a titration, a volume of a standardized solution containing a known concentration of reactant "A" is added incrementally to a sample containing an unknown concentration of reactant "B". The titration proceeds until reactant "B" is just consumed (stoichiometric completion). This is known as the **equivalence point**. At this point the number of equivalents of "A" added to the unknown equals the number of equivalents of "B" originally present in the unknown. Volumetric methods have the potential for a precision of up to 0,1%.

For volumetric methods to be useful, the reaction must reach 99% + completion in a short period of time.

In almost all cases, a buret is used to meter out the titrant. When a titrant reacts directly with an analyte (or with a reaction the product of the analyte and some intermediate compound), the procedure is termed a **direct titration**.

The alternative technique is called a **back titration**. Here, an intermediate reactant is added in excess of that required to exhaust the analyte, then the exact degree of excess is determined by subsequent titration of the unreacted intermediate with the titrant.

Regardless of the type of titration, an **indicator** is always used to detect the equivalence point.Most common are the **internal indicators**, compounds added to the reacting solutions that undergo an abrupt change in a physical property (usually absorbance or color) at or near the equivalence point. Sometimes the analyte or titrant will serve this function (auto indicating). **External indicators**, electrochemical devices such as pH meters, may also be used. Ideally, titrations should be stopped precisely at the equivalence point.

However, the ever-present random and systematic error often results in a titration **endpoint**, the point at which a titration is stopped, that is not quite the same as the equivalence point. Fortunately, the systematic error, or bias may be estimated by conducting a blank titration. In many cases the titrant is not available in a stable form of well-defined composition. If this is true, the titrant must be **standardized** (usually by volumetric analysis) against a compound that is available in a stable, highly pure form (i.e., a **primary standard).**

The basic requirements or components of a volumetric method are:

1. A standard solution (i.e., titrant) of known concentration, which reacts with the analyte with a known and repeatable stoichiometry (i.e., acid/base, precipitation, redox, complexation);
2. A device to measure the mass or volume of sample (e.g., pipet, graduated cylinder, volumetric flask, analytical balance);
3. A device to measure the volume of the titrant added (i.e., buret);
4. If the titrant-analyte reaction is not sufficiently specific, a pretreatment to remove interferents;
5. Means by which the endpoint can be determined. This may be an internal indicator (e.g., phenolphthalein) or an external indicator (e.g., pH meter).

4.6.1. Classification of volumetric methods

Volumetric methods may be based on:

- Acid/base reactions;
- Precipitation reactions;
- Complexation reactions;

Redox reactions

Table 10 presents a summary of the volumetric methods commonly used for agricultural and environmental analyses. The acid/base methods generally use a strong acid or base as a titrant with methyl orange/red (acid titration) or phenolphthalein (base titration) as the indicator. For all but acidity and alkalinity determinations, the analyte must be separated from the major cations and anions prior to titration.

Precipitative volumetric analysis relies on the formation of solid phase with a very low solubility product constant. In environmental analysis, it may be used for chloride determination. Specific indicators are used to detect excess silver or mercury.

Complexometric titrations often employ ethylenediaminetetraacetic acid or EDTA $[HOOCCH_2)_2NHCH_2CH_2NH(CH_2COOH)_2]$. This is a hexadentate ligand, which binds very strongly to many metals. For calcium and total hardness determination, a couple of specific dyes are used to determine the presence of excess cation.

Many oxidation/reduction based volumetric methods employ the iodometric method. This involves the oxidation of iodide to iodine and subsequent titration with sodium thiosulfate using starch as an indicator. Many of these employ a series of redox reactions. The permanganate method for calcium is somewhat unique in that the calcium is precipitated as the oxalate, and it is the solid-phase oxalate group, which participates in the redox reaction, not the calcium.

4.6.2. Steps in a Titration

Titrimetric analysis generally involve the following steps:

- Sampling;
- Titrant preparation;
- Standard preparation and conversion to a measurable form;
- Titrant standardization by titration of an accurately know quantity of standard;
- Sample preparation and conversion to a measurable form;
- Sample titration with the titrant solution;
- Data analysis.

Titration procedure

First, it is needed to choose volume of an unknown solution and put it in an Erlenmeyer flask.

Second, fill a buret with a standard reagent of known concentration and read the initial volume of the solution. For example, using acid/base titration, if you put an acid in the Erlenmeyer flask, you need to put a base in the buret and vice versa. A buret is a good apparatus for the determination of an equivalence point in acid-base titration because you can accurately read the volume of solution used (see Fig. 16).

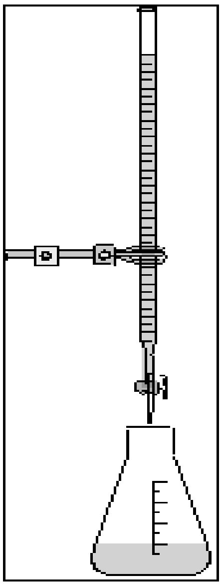


Figure 16 – Titration unit

Third, add a couple of drops of an indicator in the flask for titration. An indicator is a soluble dye that changes its color noticeably over a fairly short range of pH. Different indicators show color changes at different pH values and it is important to determine an indicator to be used according to the expected equivalence point.

If a pH meter is available, put a pH electrode in the flask.

Fourth, slightly open the cork of the buret and add the standard reagent into the unknown solution. Around the expected equivalence point of the titration, you need to drop the solution very slowly and mix the solutions very well because, around the equivalence point, just one drop of solution from the buret can make a radical pH change in the mixed solution. If the color of the solution in the Erlenmeyer flask changes, record the volume of the solution in the buret and add a few drops of the solution to make sure the equivalence point you found is correct.

4.7. Neutralization method

In the narrow sense in chemistry, neutralization means that equal amount of acids and bases in a solution react to produce salt and water. In the neutralization reaction between a strong acid and base in a solution, salt, which is produced, ionized almost perfectly so that hydrogen ions and hydroxide ions form water. Therefore, when acids and bases are equal, the hydrogen ion concentration ionizes to de-mineralized water (pH = 7), which is neutral. However, in the neutralization of a strong acid like hydrochloric acid that ionizes a large amount of hydrogen ions in the solution, and a weak base like ammonia that ionizes a small amount of hydroxide ions, the solution shows slightly acidic when the amount of the two becomes equal. On the other hand, the solution of a weak acid and strong base shows slightly alkaline when the amount of the two reaches an equal amount to achieve neutralization.

In chemical reactions, the various reacting substances always react in definite amounts. Taking the neutralization:

$$\underset{\text{1 mole}}{HCl} + \underset{\text{1 mole}}{NaOH} \rightarrow NaCl + H_2O$$

So, according to Law of equivalents 1 mole of HCl (36,5 g) will react exactly with 1 mole of NaOH (40,0 g).

Suppose we have two standard solutions: one of these (HCl) has a concentration of 1 M while the other (NaOH) also has a concentration of 1 M. Then, it follows that 1000 cm^3 of that NaOH solution will react exactly with 1000 mL of the HCl solution, since these volumes contain **equimolar amounts** (the same number of moles) of the reactants. Similarly, 500 mL of the above HCl solution will react with 1000 mL of 0,5 M NaOH, since both volumes contain 0,5 moles of the reactants. In fact, since definite amounts of acid and base are involved, we know that for the neutralization:

$$\text{acid} + \text{base} \rightarrow \text{salt} + \text{water};$$

$$\text{Amount of acid} = \text{amount of base};$$

$$\frac{\text{Volume of acid (mL)} \times \text{Normality of acid (g - eq/L)}}{1000} = \frac{\text{Volume of base (mL)} \times \text{Normality of base (g - eq/L)}}{1000}.$$

The above relationship is the basis for acid-base titrations. If we know one concentration accurately, as well as the two volumes, which neutralize each other exactly, we can easily calculate the unknown concentration.

Acid-base indicators

Indicators are weak organic acids or bases whose color is sensitive to pH or H^+ ions concentration. Chemists have a wide choice of indicators for use in the study of acids and bases and their reactions.

In a given situation they are able to choose one that has different colors at certain pH values and that changes colors over the correct pH range for a particular reaction.

The pH range over which an indicator changes color is called its transition interval.

The table 11 gives the color changes and transition intervals for a number of common acid-base indicators. As you will see the choice of indicator is based on the suitability of its transition interval for given acid-base reaction.

Table 11. Main acid-base indicators

Indicator	Color		Transition interval (pH)
	Acidic medium	Alkaline medium	
Methyl violet	Yellow	Blue	0,0-1,6
Methyl yellow	Red	Yellow	2,9-4,0
Methyl orange	Red	Yellow	3,2-4,4
Methyl red	Red	Yellow	4,8-6,0
Litmus	Red	Blue	5,5-8,0
Phenolphthalein	Colorless	Red	8,2-10,6

Indicators are generally divided into three types according to pH at which they change color.

1. Those of the first type change color at about pH equal to 7.

Such indicators include litmus. The color change interval for litmus, however, is inconveniently broad - pH 5,5 - 8,0.

This makes for considerable imprecision when acid-base reactions are being studied.

Indicators of this general type that undergo transition at about pH 7 are especially useful in the study of neutralization reactions between strong acids and strong bases.

2. Indicators of the second type change color at pH lower than 7.

Methyl orange is the example of this type. Such indicators are especially useful in study of neutralization reactions between strong acids and weak bases. These reactions produce salt solutions whose pH is lower than 7.

3. The third type of indicator changes color at pH higher than 7.

Phenolphthalein is the example. Such indicators are especially useful when study neutralization reactions between weak acids and strong bases. These reactions produce salt solutions whose pH is grater than 7.

Mixing of several different indicator solutions can make so-called universal indicators. The resulting solution can be colored depending on pH of the solution being used for test.

Strips of papers are soaked in universal indicator solution to produce pH paper. This paper can be of almost any of the colors of rainbow and thus can be a fairly accurate way for determination of different pH values.

The mechanism by which indicators operate is interesting. The indicators themselves are either weak acids or weak bases. In solution the equilibrium of the acid-base indicator can be represented by the following equation:

$$HInd \leftrightarrow H^+ + Ind^-$$

The colors that an indicator displays result from the fact that HInd and Ind^- are different colors. For example, in the case of litmus HInd is red and Ind^- is blue.

The pH of solutions can be found in way other than by use of indicators. Chemists to make rapid pH determinations generally use instrumental methods. pH - meter provides a convenient way of measuring the pH of a solution with accuracy ± 0,01 units of pH (Fig. 17).

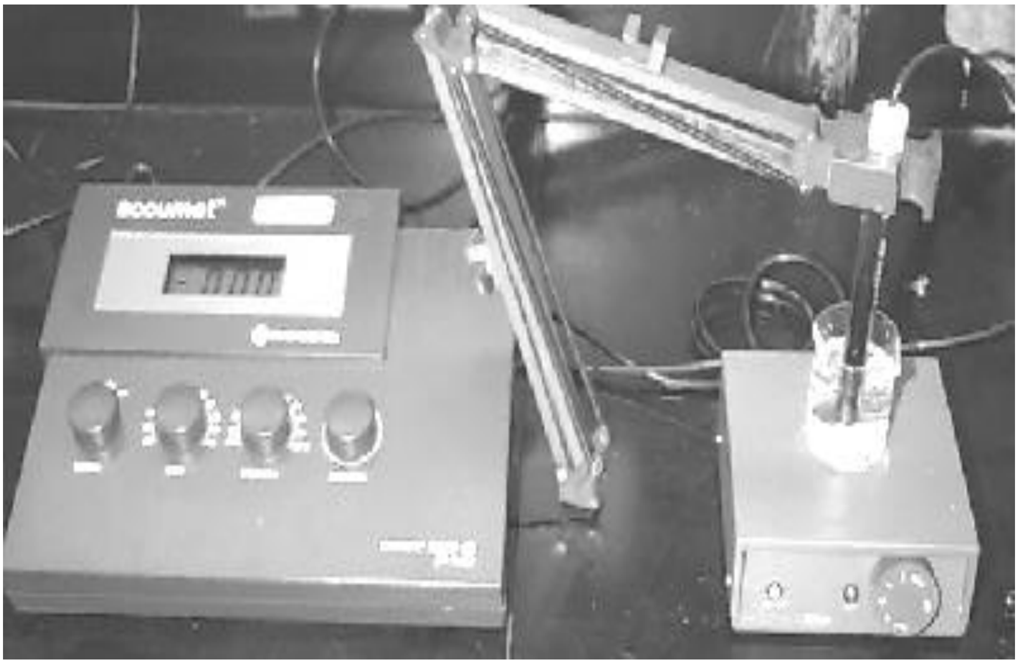


Figure 17 – pH-meter

The pH-meter measures the voltage difference between special electrode and reference electrode, which are placed in the solution. The voltage changes at the change of H^+-ion concentration. At low pH values, the concentrations of the red base form are so low that we cannot see any color. Near pH 8, the concentration of the red base form becomes significant, to the point that the human eye can detect it as a pink tinge. This deepens in color as the pH and the concentration of the red base form increase.

Indicators must be carefully chosen so that their color changes take place at the pH values expected for an aqueous solution of the salt produced in the titration.

Working solutions of neutralization method

Solutions of acids and alkalis are working solutions of method of neutralization. Solutions of H_2SO_4, HNO_3 and NaOH, KOH are used more frequent. Dissolution of exact mass of the analytically pure substance (AR) in the definite volume of solution is the most exact method of preparation of titration working solutions. But it is practically impossible in the case of the indicated acids and alkalis, because they do not respond to requests to the initial matters and solutions and their exact initial concentration is unknown. Therefore working solutions are prepared with approximate concentration in the method of neutralization, and then their exact concentration is determined by initial solutions with the prepared concentration.

More frequent for determination of exact concentration of acids is used a **borax** $\mathbf{Na_2B_4O_7\cdot 10H_2O}$ or waterless salt $\mathbf{Na_2B_4O_7}$ as a primary standard and oxalic acid $\mathbf{H_2C_2O_4\cdot 2H_2O}$ is applied for determination of exact concentration of alkalis.

Cleaning of substances for preparation of primary standards. Oxalic acid and borax are crystallized with water-hydrated molecules. They can lose the definite quantity of water at storage. Therefore if these matters were kept longer than guarantee term their recrystalization is needed.

Then borax is dissolved until satiation at the temperature 55-60°C to receive the clean preparation. After that saturated solution must be filtrated and cooled. Shallow crystals appear at interfusion by a glass stick.

Crystals of borax are filtrated, washed 2-3 times by cold water, wrung out between the sheets of filtration paper and dried at the air. If shallow crystals do not stick to the surface of glass stick at interfusion drying is considered finished. The dry reagent must be kept in glasses with corks.

Clean oxalic acid’s saturated solution is prepared in hot water like in the first case. If it is necessary solution is filtrated and cooled quickly. The selected crystals must be filtrated, washed 1-2 times by cold water and wrung out between the sheets of filtration paper. Moist powder is spread on the sheet of filtration paper and dried out at the air. Preparation is kept in glasses with corks.

Preparation of borax solution (primary standard). Borax is hydrolyzed in water at dissolution:

$$Na_2B_4O_7 + 7HOH \leftrightarrow 2\ NaOH + 4\ H_3BO_3.$$

As appearing at a hydrolysis H_3BO_3 is weak and NaOH is strong alkali solution of borax has strong alkaline the reaction and can be exactly titrated acids at the presence of methyl orange indicator. Total equation of the reaction will be:

$$Na_2B_4O_7 + 5\ HOH + 2\ HCl \leftrightarrow 2\ NaCl + 4\ H_3BO_3.$$

There is needed the exact mass for preparation of titrated solution of borax. It must be in limits from 1,7 to 2,1. When the exact mass quantity is known it is calculated the value of equivalent concentration (normality) of the prepared borax solution.

Order of preparation of solution:

- To carry taken mass of borax in a volumetric flask through a dry filtering funnel;
- Without taking out filtering funnel to wash off all crystals of salt from stream of DW;
- To wash by hot DW filtering funnel and add hot DW approximately to 2/3 measuring flask volume (100 mL);
- To obtain complete dissolution of borax mixing content of retort by circular motions. At possibility to leave flask for complete dissolution of salt;
- After cooling of solution to the room temperature to bring the level of liquid in a flask to the mark;
- To close a retort by a cork and sign the last name of student;
- To mix solution of borax carefully before the use.

Preparation of working solution of Hydrochloric acid. Order of preparation of solution:

- To take 4,5 – the 5,0 ml concentrated Hydrochloric acid by the measured cylinder or conical measuring test tube;
- To carry it to glass jar on 0,5 L;
- To rinse a cylinder by DW and outpour this water in glass jar;
- To dilute acid in glass approximately to 0,5 L by DW;
- To close glass by a cork, to mix a reagent carefully;

- To sign the last name of student and name of reagent.

Preparation of working solution of alkali. Order of preparation of solution:

- To weigh on the watch glass approximately 2 g of solid alkali;
- To carry the mass in glass jar through a dry funnel;
- To wash off all crystals of alkali without taking out funnel by the stream of DW;
- To dissolve an alkali in glass jar and bring to the general volume of solution approximately to 0,5 L by DW;
- To close glass jar by a cork, to mix a reagent carefully;
- To sign the last name of student and name of reagent.

Determination of normality of working solution of Hydrochloric acid by borax solution.

Equipment and glassware (Fig. 18):

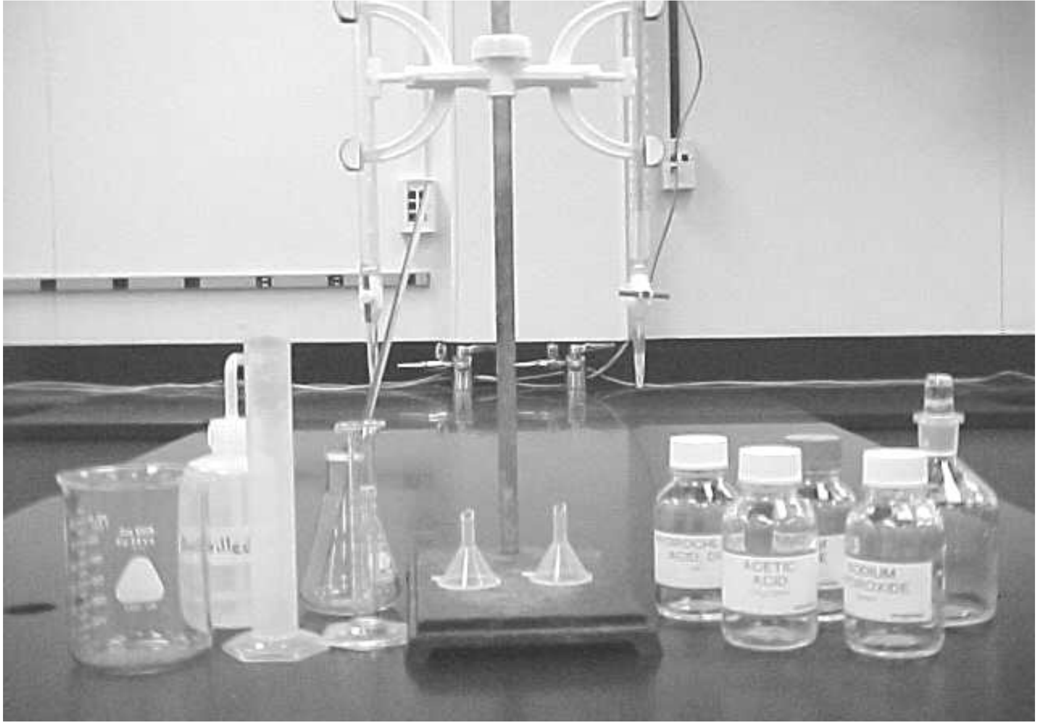


Figure 18 – Equipment for neutralization titration

- 2-3 Erlenmeyer flasks, volume 250 – 300 mL;
- Buret on 25 or 50 mL fastened on a ring stand;
- Pipet on 20 or 25 mL;
- Glass or plastic funnel of small diameter;
- Bottle with DW.

Reagents:

- Titrated solution of borax;
- Solution of HCl with approximate concentration;

- Methyl orange indicator.

Procedure:

1. Before the beginning of work to wash carefully all glassware as usual.
2. To wash buret by HCl solution.
3. To wash pipet by borax solution.
4. Using funnel to fill a buret by HCl solution and obtain absence of air bubbles in the tag of buret.
5. To take off funnel and show out the level of liquid in a buret to the zero mark.
6. To take aliquot of borax solution by a pipet in washed by distilled water Erlenmeyer flask.
7. To add 1-2 drops of methyl orange indicator to borax solution in a flask; solution will becomes yellow.
8. To put a flask with borax solution under a buret and a sheet of white paper under flask.
9. To doze HCl solution slowly with constantly mixing a liquid in a retort by smooth circular motions.
10. It is necessary to catch a moment when yellow color of solution in a flask will change on a pink from one drop of HCl.
11. To mark volume of HCl solution, which was used for titration.
12. To repeat titration of a new portion of borax solution.

TO MEMORIZE: any titration analyses must be conducted minimum three times (it is called parallel determinations). Thus the data about the volume of titrant which was used for titration are used for computations if they differ no more than on 0,1 mL. If three results have divergence more than 0,1 mL it is needed to conduct the fourth titration and etc. (until the absence of divergence). Results are presented in the table 12.

Table 12. Determination of accurate concentration of Hydrochloric acid solution used primary standard – borax

# of titration	Normality of borax solution, g-eq/L	Volume of borax in titration, mL (equal to volume of pipet)	Volume of HCl used for titration, mL	Normality of HCl, g-eq/L
1.		20,0	*Your result 1*	0,XXXX
2.		20,0	*Your result 2*	
3.		20,0	*Your result 2*	

$$\mathrm{N(HCl)} = \frac{\mathrm{N(borax)} \cdot \mathrm{V(borax)}}{\mathrm{V(HCl\ for\ titration,\ middle)}}$$

For calculation of normality of HCl solution applies middle volume from two parallel titrations which differ no more than on 0,1 mL. The value of normality is calculated within a fourth sign after a comma. A result must be added to the table 11 (to calculate for the average value of the acid volume that was used for titration).

Determination of normality of the working solution NaOH by HCl solution

Equipment and glassware: alike in a previous section.

Reagents:

- HCl solution with definite normal concentration;
- Solution of NaOH with approximate concentration;
- Methyl orange indicator.

Procedure: it is similar to the previous section, but instead of borax solution is used solution of NaOH with approximate concentration.

Results must be designed into the table 13.

Table 13. Determination of accurate concentration of NaOH

# of titration	Normality of HCl solution, g-eq/L	Volume of NaOH in titration, mL (equal to volume of pipet)	Volume of HCl used for titration, mL	Normality of NaOH, g-eq/L
1.		20,0	*Your result 1*	0,XXXX
2.		20,0	*Your result 2*	
3.		20,0	*Your result 3*	

$$\mathrm{N(NaOH)} = \frac{\mathrm{N(HCl)} \cdot \mathrm{V(HCl\ for\ titration,\ middle)}}{\mathrm{V(NaOH)}}.$$

For computation of normality of NaOH solution applies the middle volume of HCl from two parallel titrations which differ no more than on 0,1 mL.

4.7.1. Laboratory work. Determination of normality of alkali solution

Equipment and glassware: alike in a previous section.

Reagents:

- HCl solution with definite normal concentration;

- Methyl orange indicator.

Procedure: it is similar to the previous section, but instead of borax solution must be taken alkali solution. Results must be designed into the table 14.

Table 14. Determination of alkali concentration

# of titration	Normality of HCl solution, g-eq/L	Volume of HCl in titration, mL	Volume of alkali solution for determination, mL (equal to volume of pipet)	Normality of $KMnO_4$, g-eq/L
1.	From previous table, last column	*Your result 1*	20,0	0,XXXX
2.		*Your result 2*	20,0	
3.		*Your result 3*	20,0	

$$N(NaOH) = \frac{N(HCl) \cdot V(HCl\ for\ titration,\ middle)}{V(NaOH)};$$

where N (NaOH) = 0,XXXX g-eq/L.

The last result you present to teacher.

4.8. Oxidation-reduction (Redox) Titration (Redoxmetry)

4.8.1. General Principles of Redoxmetry

The methods of oxidation-reduction titration are based on quantitative oxidation or reduction of matters, which are determined. In these methods it is used reactions in which the transportation of electrons from one ion (atom, molecule) to another takes part. By this quantity of electrons, which are given back by one matter, is equal to quantity of electrons, which are accepted by another one. In consequence of such redistribution of electrons only degrees of oxidation correspondent are ions changed. Atoms or ions, which accept electrons in reaction, are oxiding agents, and that, which give back electrons are reducing agents.

Any oxidation-reduction reaction can be introduced by two separate half-reactions. Half-reaction (semi-reaction) – is the scheme of electrons transfer between two different degrees of oxidation of one element of oxidation-reduction pair. For example:

Process of oxidation $2Fe^{3+} + 2\bar{e} \rightarrow 2Fe^{2+}$ | 1 oxiding agent
Process of reduction $2I^{-} - 2\bar{e} \rightarrow I_2$ | 1 reducing agent

In such way, for realization of oxidation-reduction process simultaneous passing of reaction of oxidation and reaction of reduction is needed that is presence of oxiding agent and reducing agent in initial reagents. Therefore oxidation of one matter always is provided with simultaneous reduction of another ones and two oxidation-reduction pairs, which have different likeness with electron, always take part in oxidation-reduction reaction.

The titrant is commonly an oxiding agent although reducing titrants can be used. Efficacy of using of oxidation-reduction reaction for titration determinations depends of such factors:

1) Prevail direction of passing of processes of redistribution of passing of electrons;
2) Speed of realization of interaction of reagents;
3) Possibility of establishment of point of equivalency of reaction.

Both oxidation and reduction occur during a titration.

The equivalence point is based on the concentration of the oxidized and reduced foem of all species involved:

$$A_{ox} + B_{red} = A_{red} + B_{ox}.$$

For example,

$$Ce^{4+} + Fe^{2+} = Ce^{3+} + Fe^{3+}.$$

For a Redox titration, the equivalence point is the point where $E_{forward} = E_{reverse}$.

$E_{cell} = 0$.

Since the E values are concentration dependent, we must rely on the Nernst equation

$$E = E^{o} - \frac{0{,}059}{n}\log\frac{C_{red}}{C_{ox}}.$$

At equivalent point:

$$E^{\circ}_{A} - \frac{0{,}059}{n_A}\log\frac{[A_{red}]}{[A_{ox}]} = E^{\circ}_{B} - \frac{0{,}059}{n_B}\log\frac{[B_{red}]}{[B_{ox}]}.$$

Since $A_{red} = B_{ox}$ and $B_{red}=A_{ox}$ at the equivalence point, it can be reduce this to:

$$E_{eq} = \frac{n_A E^{\circ}_{A} + n_B E^{\circ}_{B}}{n_A + n_B}.$$

This expression is only valid for simple redox reactions, when only A_{ox} and A_{red}, B_{ox} and B_{red} are involved in the reactions.

Example 1. Determine the equivalent point for the following reaction:

$$Ce^{4+} + Fe^{2+} = Ce^{3+} + Fe^{3+}.$$

$$E^0_{Fe^{3+}/Fe^{2+}} = +\,0{,}771\,V;$$

$$E^0_{Ce^{4+}/Ce^{3+}} = +\,1{,}70\,V;$$

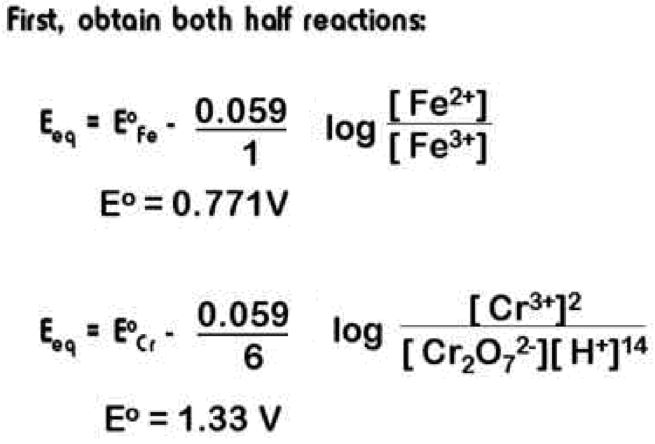
$$n_{Fe} = 1;\ n_{Ce} = 1.$$

$$E_{eq} = \frac{1{,}70\,V + 0{,}771\,V}{2} = 1{,}24\,V.$$

Determining E_{eq} becomes much more complicated for more complex system. The inclusion of one additional species, like H^+ is relatively common.

Example 2. Determine the equivalent point for the following reaction:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ = 6Fe^{3+} + 2Cr^{3+} + 7H_2O.$$



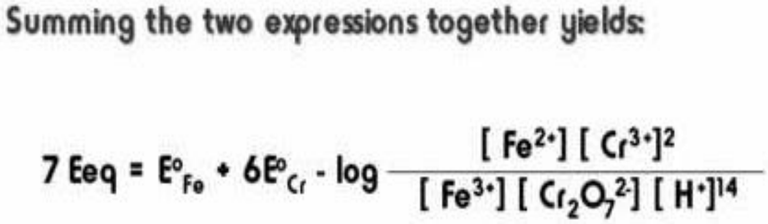
First, obtain both half reactions:

$$E_{eq} = E^o_{Fe} - \frac{0.059}{1}\ \log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$E^o = 0.771V$$

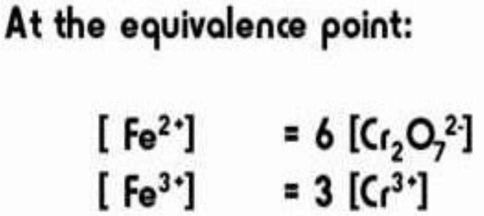
$$E_{eq} = E^o_{Cr} - \frac{0.059}{6}\ \log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

$$E^o = 1.33\ V$$



Summing the two expressions together yields:

$$7\,Eeq = E^o_{Fe} + 6E^o_{Cr} - \log\frac{[Fe^{2+}]\,[Cr^{3+}]^2}{[Fe^{3+}]\,[Cr_2O_7^{2-}]\,[H^+]^{14}}$$



At the equivalence point:

$$[Fe^{2+}] = 6\,[Cr_2O_7^{2-}]$$

$$[Fe^{3+}] = 3\,[Cr^{3+}]$$

$$E_{eq} = \frac{E^o_{Fe} + 6E^o_{Cr}}{7} - \frac{0.059}{7} \log \frac{2[Cr^{3+}]}{[H^+]^{14}}$$

$$E_{eq} = 1.25V - 8.46 \times 10^{-3} \log \frac{2[Cr^{3+}]}{[H^+]^{14}}$$

So for this reaction, the equivalence point is dependent on both $[Cr^{3+}]$ and $[H^+]$.

This explains why we commonly work in 1M acid and with dilute solutions.

If the reaction was conducted under these conditions then:

$$E_{eq} = 1.25V - 8.46 \times 10^{-3} \log \frac{2[Cr^{3+}]}{[1]^{14}}$$

E_{eq} shows only a small dependence on Cr^{3+}.

4.8.2. Quantitative Characteristic of Direction and Completeness of Passing of Oxidation-Reduction Reaction

The direction of oxidation-reduction reaction can be foreseen only on the base of quantitative characteristic of donor-acceptor, about electron, of properties of oxidation-reducing pairs, which take part in this reaction. Such characteristic is quantity of redox potential of pair, which is measured in volts and determined upon Nernst equation.

Equation of Nernst has such appearance (for every back half-reaction such: oxiding agent + n$\bar{e}$ → reducing agent):

$$E = E^\circ + \frac{RT}{nF} \cdot \ln \frac{a_{ox}}{a_{red}}$$

E – potential of half-reaction;

E^0 – standard redox potential (standard electrode potential), which are measured by activity of components of half-reaction, which is equal to 1;

R – gas constant;

T – absolute temperature;

n – number of electrons, which take part in half-reaction;

F – number of Faraday (96500);

ln – natural logarithm (2,303);

a_{ox} – activity of oxidized form;

a_{re} – activity of restored form;

At 25°C transformed formula has appearance:

$$E = E^{\circ} - \frac{0{,}059}{n} \cdot \ln \frac{a_{ox}}{a_{red}}.$$

If ions of hydrogen influence on the passing of reaction, than quantity E depends of their concentration too, but more correctly of the activity:

$$E = E^{\circ} - \frac{0{,}059}{n} \cdot \ln \frac{a_{ox}}{a_{red}} \cdot a_{H^+}.$$

For example: for the half-reaction

$$MnO_4\text{-} + 8H^+ + 5\bar{e} \rightarrow Mn^{2+} + 4H_2O$$

$$E_{MnO_4^-/Mn^{2+}} = E^{\circ} - \frac{0{,}059}{5} \cdot \lg \frac{\left[MnO_4^-\right] \cdot \left[H^+\right]^8}{\left[Mn^{2+}\right]}.$$

The Nernst equation has another appearance for reactions, which have the pair “metal – cation of metal” (for example - $Zn^{2+} + 2\bar{e} \rightarrow Zn^0$):

$$E_{Me^{\circ}/Me^{n+}} = E^{\circ} - \frac{0{,}059}{n} \cdot \lg\left[Me^{2+}\right] = E^{\circ} - \frac{0{,}059}{2} \cdot \lg\left[Zn^{2+}\right].$$

So, it is possible to solve a lot of practice problems (for example, to determine concentrations of metal ions with different oxidation numbers), which are based of oxidation-reduction methods:

a. The compulsory condition of passing of any oxidation-reduction reaction is the positive quantity of difference of potentials of half-reaction of oxiding agent and reducing agent, in other words EMS of reaction:

$$EMS = E_{ox} – E_{re}.$$

If difference between E_{ox} and E_{re} increases than EMS of reaction increases too and free energy of system decreases, and oxidation-reduction processes pass more completely.

Example 1. Calculate, in what medium reaction between $KMnO_4$ and KI is possible.

Approximate calculation can be executed by means of comparison of standard electrode potentials of half-reactions, among them are tabulated are:

a) For oxiding agent:

$MnO_4^- + 8H^+ + 5\bar{e} \rightarrow Mn^{2+} + 4H_2O$ $E^0 = + 1{,}52$ V;

$MnO_4^- + 2H_2O + 3\bar{e} \rightarrow MnO_2 + 4OH^-$ $E^0 = + 0{,}57$ V;

$MnO_4^- + \bar{e} \rightarrow MnO_4^{2-}$	$E^0 = +\,0{,}54$ V;
b) For reducing agent:	
$2I^- - 2\bar{e} \rightarrow I_2^0$	$E^0 = +\,0{,}53$ V;
$\Delta E_1 = +\,1{,}52 - 0{,}53 = +\,0{,}99$ V	Reaction will take place.
$\Delta E_2 = +\,0{,}57 - 0{,}53 = +\,0{,}04$ V	Reaction is practically impossible.
$\Delta E_3 = +\,0{,}54 - 0{,}53 = +\,0{,}01$ V	Reaction is possible.

The only reaction of oxidation of iodide-ions $KMnO_4$ in acid medium can be used for quantitative determinations.

b. It must determine the constant of balance for quantitative characteristic of possibility of realization of oxidation-reduction reaction and its suitability for titrimetric analysis, which characterize degree of transformation of initial reagents into final products, besides EMS process. For quantitative analysis only those reactions are suitable that, in which balance is displaced to side of final products, in other words approximate to 100 percent. For those reactions the constant of balance is positive number, which is equal to thousands or tens of thousands.

Example 2. Determine the constant of balance K of reaction:

$2Fe^{3+} + 2\bar{e} \rightarrow 2Fe^{2+}$ | 1 oxiding agent;

$2I^- - 2\bar{e} \quad \rightarrow I_2^0$ | 1 reducing agent.

Probably, that balance in present system come only by equivalency of potentials both half-reactions:

$$E_{Fe^{3+}/Fe^{2+}} = E^0_{I_2^0/2I^-};$$

for half-reaction $2Fe^{3+} + 2\bar{e} \rightarrow 2Fe^{2+}$:

$$E_{Fe^{3+}/Fe^{2+}} = E^0_{Fe^{3+}/Fe^{2+}} - \frac{0{,}059}{2}\lg\frac{a^2_{Fe^{3+}}}{a^2_{Fe^{2+}}};$$

for half-reaction $2I^- - 2e \rightarrow I_2^0$:

$$E_{I_2^{\circ}/2I^-} = E^0_{I_2^{\circ}/2I^-} - \frac{0{,}059}{2}\lg\frac{a_{I_2^{\circ}}}{a^2_{I^-}}.$$

So, in the moment of balance:

$$E^{\circ}_{Fe^{3+}/Fe^{2+}} - \frac{0{,}059}{2}\lg\frac{a^2_{Fe^{3+}}}{a^2_{Fe^{2+}}} = E^{\circ}_{I_2^{\circ}/2I^-} - \frac{0{,}059}{2}\lg\frac{a_{I_2^{\circ}}}{a^2_{I^-}};$$

$$E_{Fe^{3+}/Fe^{2+}} - E_{I_2^0/2I^-} = \frac{0{,}059}{2}\lg\frac{a_{I_2^{\circ}}}{a^2_{I^-}} - \frac{0{,}059}{2}\lg\frac{a^2_{Fe^{3+}}}{a^2_{Fe^{2+}}};$$

$$E_{Fe^{3+}/Fe^{2+}} - E_{I_2^{\circ}/2I^-} =$$

$$= \frac{0{,}059}{2}\left(\lg \frac{a_{I_2^{\circ}}}{a^2_{I^-}} - \lg \frac{a^2_{Fe^{3+}}}{a^2_{Fe^{2+}}} \right) = \frac{0{,}059}{2} \lg \frac{a_{I_2^{\circ}} \cdot a^2_{Fe^{3+}}}{a^2_{I^-} \cdot a^2_{Fe^{2+}}};$$

for reaction: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2^0$:

$$K = \frac{a_{I_2^{\circ}} \cdot a^2_{Fe^{3+}}}{a^2_{I^-} \cdot a^2_{Fe^{2+}}};$$

then $E^{\circ}_{Fe^{3+}/Fe^{2+}} - E^{\circ}_{I_2^0/2I^-} = \frac{0{,}059}{2} \lg K$;

$$\lg K = \frac{2\left(E^{\circ}_{Fe^{3+}/Fe^{2+}} - E^{\circ}_{I_2^0/2I^-} \right)}{0{,}059};$$

$$E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0{,}77\,V;\ E^{\circ}_{I_2^{\circ}/2I^-} = 0{,}54\,V;\ Keq = 10^8.$$

Such great value of equilibrium constant is evidence of practically total displacement of balance of reaction to side of final products, in other words present reaction passes to the end and can be used for quantitative determination of concentration of solution of salt of iron (III) by titration of solution of iodine.

Curves of Oxidation-reduction titration

The titration or oxiding agents or reducing agents is accompanied by the change of redox potential of the system. The changes of potential of the system depending on quantity of titrate, which is added to determined chemical agent, is the curve of oxidation-reduction titration in graphic expression.

The character of the curve of titration has a sense for determination of point of equivalency of reaction and for correct choice of indicator.

Constructions of such curves are divided into three parts for convenience:

1. The area to point of equivalency;
2. The point of equivalency;
3. The area after point of equivalency.

For example, for construction of the curve of titration of salt of Fe^{3+} by solution of $KMnO_4$ in acid medium by reaction:

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

$Fe^{2+} - \bar{e} \rightarrow Fe^{3+}$ | 5 oxiding agent;

$Mn^{7+} + 5\bar{e} \rightarrow Mn^{2+}$ | 1 reducing agent

from these considerations:

1. ORP (oxiding-reducing potential) of the system to the point of equivalency, when Fe^{2+} is in plenty, is calculated by the equation:

$$E_{Fe^{3+}/Fe^{2+}} = E^{\circ}_{Fe^{3+}/Fe^{2+}} - \frac{0{,}059}{2} \lg \frac{a^2_{Fe^{3+}}}{a^2_{Fe^{2+}}};$$

2. Calculations have another appearance after the point of equivalency, when potential of the system is determined by surplus of titrate:

$$E_{MnO_4^-/Mn^{2+}} = E^{\circ}_{MnO_4^- + 8H^+/Mn^{2+}} - \frac{0{,}059}{5} \lg \frac{\left[MnO_4^-\right] \cdot \left[H^+\right]^8}{\left[Mn^{2+}\right]};$$

3. In the point of equivalency:

$$E = \frac{E^{\circ}_{Fe^{3+}/Fe^{2+}} + E^{\circ}_{MnO_4^- + 8H^+/Mn^{2+}}}{2}.$$

Titrating Solutions in Methods of Redoxmetry and Indicators

The methods of oxidation-reduction titration, as with another methods volumetric analysis, are based on using of titrating solutions. And the classification of oxidation-reduction methods of analysis is realized by throughout the oxiding agent, which, as a rule, isn't initial reagent of analysis because of present of admixtures in compound or change of concentration of chemical agent at the time of preparation of solutions.

Table 15. Characteristics of the most extended methods of Redoxmetry

Method	Oxiding agent	Initial reagents of the method
Permanganatometry	$KMnO_4$	$H_2C_2O_4 \cdot 2H_2O$ $Na_2C_2O_4$ $(NH_4)_2C_2O_4 \cdot H_2O$
Iodometry	Solution of I_2	$Na_2S_2O_3 \cdot 5H_2O$ (as a rule secondary standard) $K_2Cr_2O_7$ such as initial standard for the solution) $Na_2S_2O_3$
Dichromatometry	$K_2Cr_2O_7$	$K_2Cr_2O_7$

One must remember, that compounds must be extra quality, by preparation of titrating solutions out of initial reagents. If it is necessary pass their recrystallization. Besides we must be sure, that their mixture completely complies with formula.

In any case it is necessary to calculate the weights of initial reagents for preparing of their solutions (initial standard) or working solutions of oxiding agents and reducing agents (secondary process).

The equation m = N·V, where N and V – adjusted values, is underlying of calculation of weight, and one must know such rule, besides formula of compound: “Gram-equivalent of oxiding agent or reducing agent in reaction is equal to ratio of their molar mass to the number of electrons, which are distributed by the present chemical agent in oxidation-reduction reaction” for calculation of equivalent (E).

As far as types of oxidation-reduction reactions in methods of permanganatometry, iodometry and dichromatemetry these calculations are the following:

The types of reactions	The calculation of equivalency
$2\,KMnO_4 + 5\,H_2C_2O_4 + 3\,H_2SO_4 =$ $= K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O.$ $Mn^{7+} + 5\bar{e} \rightarrow Mn^{2+} \mid 2$ $2C^{3+} - 2\bar{e} \rightarrow 2C^{4+} \mid 5$	$E_{KMnO_4} = \frac{M_{KMnO_4}}{5};$ $E_{H_2C_2O_4} = \frac{M_{H_2C_2O_4 \cdot 2H_2O}}{2}.$
$3\,MnSO_4 + 2\,KMnO_4 + 2H_2O =$ $= 5MnO_2 + K_2SO_4 + 2H_2SO_4.$ $Mn^{7+} + 3\bar{e} \rightarrow Mn^{4+} \mid 2$ $Mn^{2+} - 2\bar{e} \rightarrow Mn^{4+} \mid 3$	$E_{MnSO_4} = \frac{M_{MnSO_4}}{2};$ $E_{KMnO_4} = \frac{M_{KMnO_4}}{3}.$
$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$ $4S^{+2} - 2\bar{e} \rightarrow 4S^{+2.5} \mid 1$ $I_2{}^{0} + 2\bar{e} \rightarrow 2I^{-} \mid 1$	$E_{Na_2S_2O_3} = \frac{M_{Na_2S_2O_3 \cdot 5H_2O}}{1};$ $E_{I_2} = \frac{M_{I_2}}{2}.$

The point of equivalency is determined with the using of indicators, as like of any titrimetric method. We define some types of indicators:

1. Indicator is any reagent, which is used for titration or forms following the titration.

For example:

Method	Indicator	Medium	Reaction and color of reagents
Permanganatometry	$KMnO_4$	Acid	MnO_4^- (violaceous) + $5\bar{e}$ + $8H^+ \rightarrow$ Mn^{2+}(colorless)+$4H_2O$
		Neutral	MnO_4^- (violaceous)+$3\bar{e}$ + $2H_2O \rightarrow$ MnO_2 (brown sediment)+$4OH^-$
		Alkaline	MnO_4^- (violaceous) + $\bar{e} \rightarrow$ MnO_4^{2-}(green)

On practice by realization of oxidation-reduction titration, it must consider not only the possibility of passing of reaction, but also the possibility of visual perception of change of color of indicator. So human’s eye reacts most sensitively in permanganatometry to the change of red-violaceous color on colorless, and vice versa.

2. Indicator is a compound, which is able to enter into specific reaction with titrating solution or product of its reduction or oxidation.

This is, for example, starch, which is an indicator on the elementary (free) iodine (intensive blue). The point of equivalency can be fixed by appearance of color or by its disappearance. The concentration of iodine in solution, which is equal $2 \cdot 10^{-7}$ M, produces noticeable color.

3. Redox-indicators are oxidation-reducing pairs, where oxidized and reduced forms differ in color. At that, change of color happen only when, then fixed value of oxidation-reduction potential of the system is reached. There is necessary condition order to potential of change their color concurs with sudden change of titration on the curve of titration, but the best – with the point of equivalency by use such indicators.

For example:

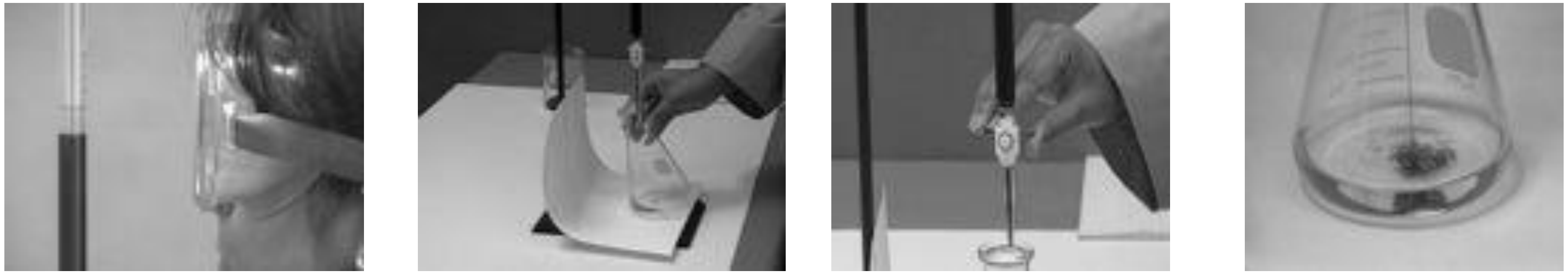
a) dephinileamine and its derivatives. Change of color happen from colorless to blue color by $E = +0{,}77$ V;

b) Phenileantranile acid. The change of color happen from colorless to blue color by $E = +1{,}08$ V. It is used for determination of Mo^{6+} in method of vanadiummetry;

c) Ferroine. Change of color happen from red to pale-blue color by $E = +1{,}06$ V. It is used for determination of reducing agents by strong oxiding agents.

Procedure

In a titration it measures the quantity of one reactant that is required to consume all of another reactant. To accomplish this you measure the volume of liquid released from the buret during the procedure. The initial level of the liquid in the buret is observed and recorded. The flask containing the sample to be titrated is placed under the buret. When the purple titrant enters the flask it reacts with the colorless sample. The products of the reaction are colorless. The titrant is a purple solution. The titrant solution in the buret is added to the sample solution in the flask. At this stage all of the added titrant has reacted within the flask. We know this because the solution in the flask has reverted back to being clear and colorless. Now we are at the end point of the titration where enough titrant has been added from the buret to react with all of the reactant in the flask and the solution's color has changed slightly due to a slight excess of titrant. At this point we can take our final reading (see Fig. 19).



a
Initial reading.

b
Placing the flask with sample.

c
Adding titrant...

d
... to the sample.

e
One final squirt.

f
Slightly pink - the end point.

g
Final reading.

Figure 19 – Permanganatometry titrating process by steps

4.8.3. Laboratory work. Determination of Iron (II) content in More's salt

Equipment:

- 250 mL Erlenmeyer flasks;
- 20 mL pipet;
- Buret;
- Buret clamp;
- 100 mL graduated cylinder;
- Ring stand;
- Hot plate;
- Laboratory thermometer.

Reactants:

- Initial standard solution of oxalatic acid $H_2C_2O_4 \cdot 2H_2O$ of known concentration for titration in acidic medium (for example, 0,0500 N);
- Solution of $KMnO_4$ of approximately 0,05 N;
- Solution of 2 N sulfuric acid;
- DW (distilled water).

Determination of accurate (precise) concentration of $KMnO_4$

We have a solution of $KMnO_4$, a strong oxidizing agent. We know that its concentration is approximately 0,05 N, but we cannot prepare a solution of it whose concentration is accurately known. This is because the $KMnO_4$ will react with small amounts of organic material present in the water when the solution is first prepared. As a result, the concentration will never be as high as calculated. We are going to react a known volume of $KMnO_4$ with a known volume of a reducing agent oxalatic acid $H_2C_2O_4 \cdot 2H_2O$. The concentration of the last solution is accurately known.

We will perform stoichiometric calculations to determine the concentration of the potassium permanganate. The combination of the two solutions gives the next equations:

$$5\ H_2C_2O_4 \cdot 2H_2O + 2\ KMnO_4 + 3\ H_2SO_4 = 10\ CO_2 + 2\ MnSO_4 + \\ + K_2SO_4 + 18\ H_2O; \qquad (8)$$

$$Mn^{7+} + 5\bar{e} \rightarrow Mn^{2+} \quad \left|\, 2 \right. \text{ oxiding agent;}$$

$$2C^{3+} - 2\bar{e} \rightarrow 2C^{4+} \quad \left|\, 5 \right. \text{ reducing agent.}$$

If precise concentration of oxalic acid is known and reacted volumes of permanganate and oxalic acid solutions, the precise concentration of $KMnO_4$ may be calculated according Law of Equivalents:

$$N(KMnO_4) = \frac{N(H_2C_2O_4) \cdot V(H_2C_2O_4)}{V(KMnO_4)} \qquad (9).$$

Procedure. Clean pipet, buret and Erlenmeyer flasks, as described above.

Add 20 mL of oxalic acid solution from measuring pipet to 250-300 mL Erlenmeyer flask. Acidify this solution adding 20 mL of 2 N H_2SO_4 using graduated cylinder. Add near 40 mL of DW. Heat prepared solution to 70-80°C (control temperature by laboratory thermometer). **BE CAREFUL, NOT BOIL SOLUTION** (because oxalic acid decomposes at 100°C)!

Using a buret, slowly add the $KMnO_4$ solution to hot solution in flack. Reaction (1) will occur. $KMnO_4$ acts as its own indicator. That is, at the start of the titration the deep violet color of MnO_4^- will be lost because it is changing to Mn^{+2}, but as soon as there is no more oxalic acid in the solution for the MnO_4^- to react with, the MnO_4^- will remain in the reaction solution. The slightly pink color of the dilute solution MnO_4^- indicates the end of the reaction. This color must safe during at least 1 min. This is known as the "end point" or equivalence point of the titration.

The procedure of titration is repeated two times or more. The results of so-called parallel titrations (volumes of $KMnO_4$ used for reaction (8)) must distinguish one from other not more than 0,1 mL (one point of buret).

Results of experiment present in the form of table 16:

Table 16. Determination of accurate concentration of Permanganate solution used primary standard – oxalic acid

# of titration	Normality of oxalic acid solution, g-eq/L	Volume of oxalic acid in titration, mL (equal to volume of pipet)	Volume of permanganate solution used for titration, mL	Normality of $KMnO_4$, g-eq/L
1.	0,0500	20,0	*Your result 1*	0,XXXX
2.	0,0500	20,0	*Your result 2*	
3.	0,0500	20,0	*Your result 3*	

Example. For 3 parallel titrations of 20 mL of 0,0500 N oxalic acid it was used 10,2; 10,4; 10,5 mL of $KMnO_4$ solution correspondingly. What's accurate concentration of permanganate solution?

We take for calculation only two results - 10,4 and 10,5 mL distinguished one from other on 0,1 mL. Evidently, result 10,2 mL was erroneous. So, average reading of titration is:

$$V\ (KMnO_4)_{average} = \frac{V_1 + V_2}{2} = \frac{10,4 + 10,5}{2} = 10,45\,\text{mL}.$$

According equation (9), accurate concentration of permanganate solution is equal to:

$$N(KMnO_4) = \frac{N(H_2C_2O_4) \cdot V(H_2C_2O_4)}{V(KMnO_4)} =$$

$$\frac{0{,}0500 g - eq/L \cdot 20{,}0\,mL}{10{,}45\,mL} = 0{,}0957\ g\text{ - }eq/L.$$

Determination of Iron (II) concentration in the solution of More's salt

More's salt is a double salt - iron (II) ammonium sulfate hexahydrate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) included ions of Fe (II). The last one may reacts with potassium permanganate in acidic medium:

$$10\ Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O + 2\ KMnO_4 + 8\ H_2SO_4 = 5\ Fe_2(SO_4)_3 + 2\ MnSO_4 + 10\ (NH_4)_2SO_4 + K_2SO_4 + 68\ H_2O; \qquad (10)$$

$$Mn^{7+} + 5\bar{e} \rightarrow Mn^{2+} \quad | 2 \text{ oxiding agent;}$$

$$2Fe^{2+} - 2\bar{e} \rightarrow 2Fe^{3+} \quad | 5 \text{ reducing agent.}$$

This reaction isn't heating, because ion Fe (II) may oxidizes by air oxygen transformed to Fe (III) with rising of temperature.

Procedure. Add 20 mL of More's salt solution (**according to your variant of task)** with unknown concentration used measuring pipet to 250-300 mL Erlenmeyer flask. Acidify this solution adding 20 mL of 2 N H_2SO_4 using graduated cylinder. Add near 40 mL of DW. **BE CAREFUL, DON'T HEAT SOLUTION**!

Using a buret, slowly add the $KMnO_4$ solution to hot solution in flack. Reaction (9) will occur. $KMnO_4$ acts as its own indicator. The slightly pink color of the dilute solution MnO_4^- indicates the end of the reaction. This color must safe during at least 1 min. The procedure of titration repeats two times or more as described above.

Results of experiment present in the form of table 17:

Table 17. Determination of concentration of Iron (II) in More's salt solution

# of titration	Normality of $KMnO_4$ solution, g-eq/L	Volume of $KMnO_4$ in titration, mL	Volume of More's salt solution for determination, mL (equal to volume of pipet)	Normality of $KMnO_4$, g-eq/L
1.	From previous table, last column	*Your result 1*	20,0	0,XXXX
2.		*Your result 2*	20,0	
3.		*Your result 3*	20,0	

Calculate the concentration of Fe^{+2} present in the unknown solution:

$$N\,(Fe^{2+}) = \frac{N(KMnO_4)\cdot V(KMnO_4\ \text{avarage for titration of More's salt})}{V(\text{More's salt solution})};$$

where N (Fe^{2+}) = 0,XXXX g-eq/L.

The last result you present to teacher.

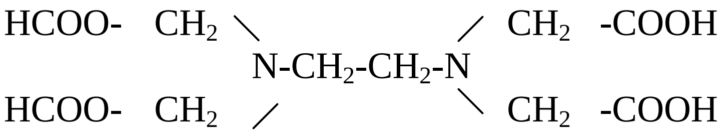
DON’T FORGET! Empty unused $KMnO_4$ solution back into the reagent bottle. Rinse your buret several times with water.

4.9. Complexonometry (Chelatometry)

Reactions of complex or weak-dissociated compounds are the base of methods for determination of same ions in solution.

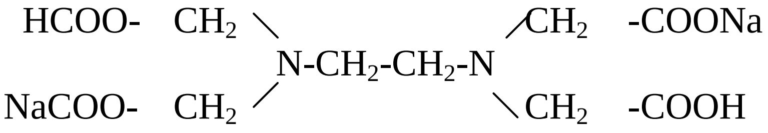
The most important one in titrimetric analysis has a complexing of metals ions with halide- or pseudo-halide ions (SCN^-, CN^-), and with group of polyamine carboxylic acids (chelators). The most popular chelators are the so-called complexon II, III:

Complexon II – - ethylene diammine tetraacetic acid, EDTA, H_4Y:



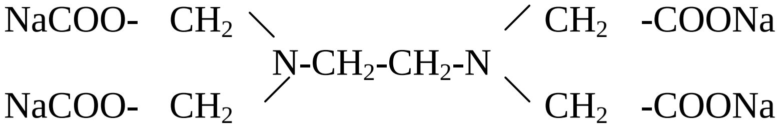
$$\begin{array}{lcl} HCOO\text{-}\ CH_2 \diagdown & & \diagup\ CH_2\ \text{-}COOH \\ & N\text{-}CH_2\text{-}CH_2\text{-}N & \\ HCOO\text{-}\ CH_2 \diagup & & \diagdown\ CH_2\ \text{-}COOH \end{array}$$

Complexon III - disodium ethylene diammine tetraacetate, Trilon, NaEDTA, Na_2H_2Y:



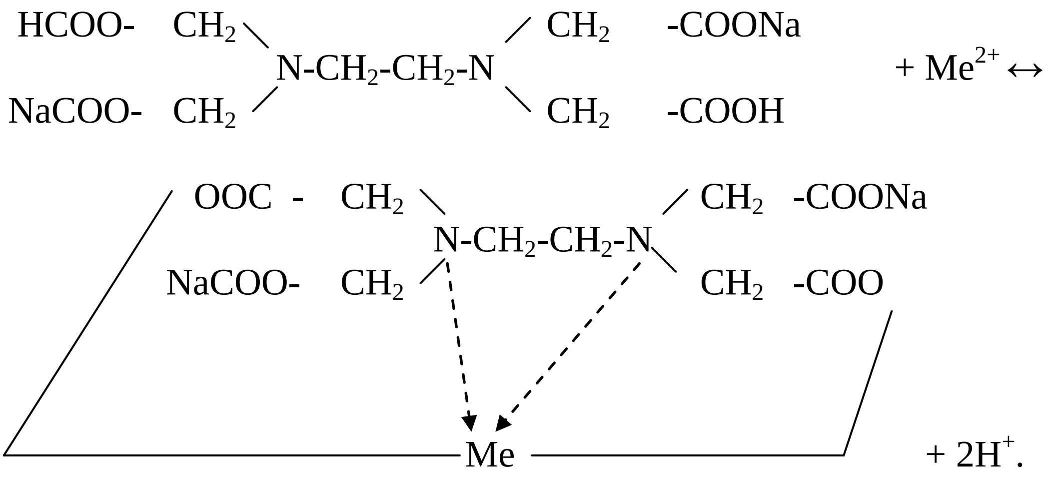
$$\begin{array}{lcl} HCOO\text{-}\ CH_2 \diagdown & & \diagup CH_2\ \text{-}COONa \\ & N\text{-}CH_2\text{-}CH_2\text{-}N & \\ NaCOO\text{-}\ CH_2 \diagup & & \diagdown CH_2\ \text{-}COOH \end{array}$$

Complexon IV - tetrasodium ethylene diammine tetraacetate, NaEDTA, Na_4Y:



$$\begin{array}{lcl} NaCOO\text{-}\ CH_2 \diagdown & & \diagup\ CH_2\ \text{-}COONa \\ & N\text{-}CH_2\text{-}CH_2\text{-}N & \\ NaCOO\text{-}\ CH_2 \diagup & & \diagdown\ CH_2\ \text{-}COONa \end{array}$$

The most commonly used regent for this method Trilon B may forms a very stable complex compound with a great number of cations (alkaline metals, copper, zinc, iron, manganese at all) according to the next reaction:



Advantages of chelatometry:

- High sensitivity (up to 10^{-2} Mol/L);
- High rate of chemical reaction;
- Stoichiometric relationship of reagents;
- High selectivity.

Essentially, Trilon B may dissociates by steps depends pH:

$$Na_2H_2Y \leftrightarrow 2Na^+ + H_2Y^{2-}; pH = 4{,}5;$$
$$H_2Y^{2-} \leftrightarrow H^+ + HY^{3-}; pH = 8{,}5;$$
$$HY^{3-} \leftrightarrow H^+ + Y^{4-}; pH > 9.$$

Different cations form stable complexes with Trilon B depending on their nature. For example, triple-charged cations form stable complexes when pH very low (1-3), while cations of alkaline earth metals – at pH 10.

Determination of titration endpoint – using special metallochromical indicators. They are a weak complexing agents made own color and formed color complexing compounds with metal cations. Last ones have a weak stability. One of such indicators is an Eriochrome black T. Its own color in solution is sky-blue, when color of his complexes with metals is wine-red. In general, schemes of titration processes are:

$$Me^{n+} + \underset{\text{Sky-blue solution}}{Ind} \leftrightarrow \underset{\text{wine-red solution}}{MeInd^{n+}}$$

$MeInd^{n+}$	+ EDTA	↔	MeEDTA	+ Ind
Wine-red solution	Colorless solution		Colorless solution	Sky-blue solution

4.9.1. Laboratory work. Determination of Total Water Hardness

Equipment:

- 250 mL Erlenmeyer flasks;
- 20 mL pipet;
- Buret;
- Buret clamp;
- 10 mL graduated cylinder;
- 100 mL graduated cylinder;
- Ring stand.

Reactants:

- Initial standard solution of zinc sulfate $ZnSO_4$ of known concentration (for example, 0,0500 N);
- Solution of Trilon B of approximately 0,05 N;
- Ammonium Buffer Solution (pH =10);
- Indicator – solid Eriochrome black T;
- DW (distilled water).

Determination of accurate (precise) concentration of Trilon B solution

Solid Trilon B end its solutions are not stable. Therefore in chelatometry initial standards are sulfates of zinc or magnesium (sometimes metallic zinc). Reaction between Trilon B and $ZnSO_4$ must be occurred when pH 10. Such value of pH can be maintained by adding of **buffer solutions**. Buffers are the solutions contained mixture of a weak acid and its salt or weak base and its salt. When adding to such solutions a strong acid or strong base pH doesn’t change practically.

Procedure.

To prepare a buret, pipet and titration flask to analysis as usual. To fill out a buret by a Trilon B solution. Take an aliquot of $ZnSO_4$ standard solution by pipet and transport it into a titration flask. Add 5 mL of buffer solution to flask (using 10 mL graduated cylinder). Add a few crystals of indicator, to mix solution. It must be transparent wine-red color.

Add a Trilon B solution from buret to the change of solution color to sky-blue after adding of one or two last drops of titrant.

Results of experiment present in the form of table 18:

Table 18. Determination of accurate concentration of Trilon B solution used primary standard – solution of zinc sulfate

# of titration	Normality of zinc sulfate solution, g-eq/L	Volume of zinc sulfate for titration, mL (equal to volume of pipet)	Volume of Trilon B solution used for titration, mL	Normality of Trilon B solution, g-eq/L
1.	0,0500	20,0	*Your result 1*	0,XXXX
2.	0,0500	20,0	*Your result 2*	
3.	0,0500	20,0	*Your result 3*	

To calculate an accurate concentration of Trilon B according to the next formula:

$$N\,(\text{Trilon B}) = \frac{N\,(ZnSO_4)\cdot V\,(ZnSO_4)}{V\,(\text{Trilon B})}, \text{ where}$$

N ($ZnSO_4$) – normality of initial standard solution of zinc sulfate, g-eq/L;

V (($ZnSO_4$) – volume of zinc sulfate solution (is equal to the volume of pipet), mL;

V (Trilon B) – volume of Trilon B for titration, mL.

All aspects of water hardness

Sources of Hardness Minerals in Drinking Water

Water is a good solvent and picks up impurities easily. Pure water - tasteless, colorless, and odorless - is often called the universal solvent. When water is combined with carbon dioxide CO_2 to form very weak carbonic acid H_2CO_3, an even better solvent results. As water moves through soil and rock, it dissolves very small amounts of minerals and holds them in solution. Calcium and magnesium dissolved in water are the two most common minerals that make water "hard." The degree of hardness becomes greater as the calcium and magnesium content increases and is related to the concentration of multivalent cations dissolved in the water.

Indications of Hard Water

Hard water interferes with almost every cleaning task from laundering and dishwashing to bathing and personal grooming. Clothes laundered in hard water may look dingy and feel harsh and scratchy. Dishes and glasses may be spotted when dry. Hard water may cause a film on glass shower doors, shower walls, bathtubs, sinks, faucets, etc. Hair washed in hard water may feel sticky and look dull. Water flow may be reduced by deposits in pipes.

Dealing with hard water problems in the home can be a nuisance. The amount of hardness minerals in water affects the amount of soap and detergent necessary for cleaning. Soap used in hard water combines with the minerals to form a sticky soap curd. Some synthetic detergents are less effective in hard water because the active ingredient is partially inactivated by hardness, even though it stays dissolved. Bathing with soap in hard water leaves a film of sticky soap curd on the skin. The film may prevent removal of soil and bacteria. Soap curd interferes with the return of skin to its normal, slightly acid condition, and may lead to irritation. Soap curd on hair may make it dull, lifeless and difficult to manage.

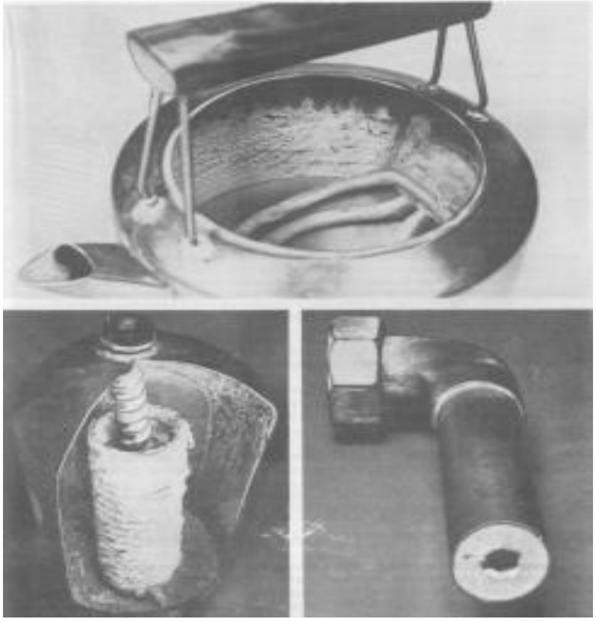


Figure 20 – Indicators of hard water

When doing laundry in hard water, soap curds lodge in fabric during washing to make fabric stiff and rough. Incomplete soil removal from laundry causes graying of white fabric and the loss of brightness in colors. A sour odor can develop in clothes. Continuous laundering in hard water can shorten the life of clothes. In addition, soap curds can deposit on dishes, bathtubs and showers, and all water fixtures (Fig. 20).

Hard water also contributes to inefficient and costly operation of water-using appliances. Heated hard water forms a scale of calcium and magnesium minerals that can contribute to the inefficient operation or failure of water-using appliances. Pipes can become clogged with scale that reduces water flow and ultimately requires pipe replacement.

Potential Health Effects

Hard water is not a health hazard. In fact, the USA National Research Council (National Academy of Sciences) states that hard drinking water generally contributes a small amount toward total calcium and magnesium human dietary needs. They further state that in some instances, where dissolved calcium and magnesium are very high, water could be a major contributor of calcium and magnesium to the diet. Researchers have studied water hardness and cardiovascular disease mortality. Such studies have been "epidemiological studies," which are statistical relationship studies. While some studies suggest a correlation between hard water and lower cardiovascular disease mortality, other studies do not suggest a correlation. The National Research Council states that results at this time are inconclusive and recommends that further studies should be conducted.

Water hardness is classified by different ways. For example, types of classification in different countries are presented in table 19.

Table 19. Classification of fresh water according water hardness

Water hardness, mg-eq/L	**Ukraine**	**Germany**	**USA**
0 – 1,5	**Soft (0 – 4)**	**Soft (0 – 1,6)**	**Very soft (0 – 1,5)**
1,5 – 1,6			**Slightly hard (1,5 - 3,0)**
1,6 – 2,4		**Hard (1,6 – 2,4)**	
2,4 – 3,0		**Moderately hard (2,4 – 3,6)**	
3,0 – 3,6			**Hard (3,0 – 6,0)**
3,6 – 4,0		**Hard (3,6 – 6,0)**	
4,0 – 6,0	**Moderately hard (4 – 8)**		
6,0 – 8,0		**Very hard (> 6)**	**Very hard (> 6)**
8,0 – 9,0	**Hard (8 – 12)**		
9,0 – 12,0			
More than 12,0	**Very hard (> 12)**		

Treatment

There are two ways to help control water hardness: use a packaged water softener or use a mechanical water-softening unit.

Packaged water softeners are chemicals that help control water hardness. They fall into two categories: precipitating and non-precipitating.

Precipitating water softeners include washing soda and borax. These products form an insoluble precipitate with calcium and magnesium ions. The mineral ions then cannot interfere with cleaning efficiency, but the precipitate makes water cloudy and can build up on surfaces. Precipitating water softeners increase alkalinity of the cleaning solution and this may damage skin and other materials being cleaned.

Non-precipitating water softeners use complex phosphates to sequester calcium and magnesium ions. There is no precipitate to form deposits and alkalinity is not increased. If used in enough quantity, non-precipitating water softeners will help dissolve soap curd for a period of time.

Mechanical water softening units can be permanently installed into the plumbing system to continuously remove calcium and magnesium. Water softeners operate on the ion exchange process. In this process, water passes through a media bed, usually sulfonated polystyrene beads. The beads are supersaturated with sodium. The ion exchange process takes place as hard water passes through the softening material. The hardness minerals attach themselves to the resin beads while sodium on the resin beads is released simultaneously into the water. When the resin becomes saturated with calcium and magnesium, it must be recharged. The recharging is done by passing a salt (brine) solution through the resin. The sodium replaces the calcium and magnesium, which are discharged in the wastewater. Hard water treated with an ion exchange water softener has sodium added. According to the Water Quality Association (WQA), the ion exchange softening process adds sodium at the rate of about 8 mg/liter for each grain of hardness removed per gallon of water.

For example, if the water has a hardness of 10 grains per gallon, it will contain about 80 mg/liter of sodium after being softened in an ion exchange water softener if all hardness minerals are removed.

Because of the sodium content of softened water, some individuals may be advised by their physician, not to install water softeners, to soften only hot water or to bypass the water softener with a cold water line to provide unsoftened water for drinking and cooking; usually to a separate faucet at the kitchen sink.

Softened water is not recommended for watering plants, lawns, and gardens due to its sodium content.

Although not commonly used, potassium chloride can be used to create the salt brine. In that case potassium rather than sodium is exchanged with calcium and magnesium.

Before selecting a mechanical water softener, test water for hardness and iron content. When selecting a water softener, the regeneration control system, the hardness removal capacity and the iron limitations are three important elements to consider.

There are three common regeneration control systems. These include a time-clock control (you program the clock to regenerate on a fixed schedule); water meter control (regenerates after a fixed amount of water has passed through the softener); and hardness sensor control (sensor detects hardness of the water leaving the unit, and signals softener when regeneration is needed).

Hardness removal capacity, between regenerations, will vary with units. Softeners with small capacities must regenerate more often. Your daily softening need depends on the amount of water used daily in your household and the hardness of your water. To determine your daily hardness removal need, multiply daily household water use (measured in gallons) by the hardness of the water (measured in grains per gallon).

Example: 400 gallons used per day X 15 grains per gallon hardness =
= 6,000 grains of hardness must be removed daily.

Iron removal limitations will vary with water softener units. If the iron level in your water exceeds the maximum iron removal capacity recommended by the manufacturer of the unit you are considering, iron may foul the softener, eventually causing it to become plugged.

There are different traditions for expressing of water hardness (see table 20). In Ukraine units for water hardness is called mg-eq/L (milligrams-equivalents per litre). This unit shows quantity of milliequivalents of calcium and magnesium in one litre of water.

Determination of Total Water Hardness

Procedure.

1. To prepare a buret, pipet and titration flask to analysis as usual.
2. To fill out a buret by a Trilon B solution.
3. To take 100 mL of analyzable water by 100 mL graduated cylinder and transport it into a titration flask.
4. To add 5 mL of buffer solution to flask.

Table 20. Conversion of water hardness units

Water Hardness Unit Definition	**International recommended, mmol/litre**	**Physical measures, mval/litre**	**United States, ppm**	**English, °e**	**French, °f**	**Germany, °dH**
	100 mg $CaCO_3$ per 1000 mL water	28 mg CaO or 50 mg $CaCO_3$ per 1000 mL water	1 part $CaCO_3$ per million = 1 mg $CaCO_3$ per 1000 mL water	1 grain $CaCO_3$ per gallon = 14,3 mg $CaCO_3$ per 1000 mL water	10 mg/ $CaCO_3$ per 1000 mL water	10 mg/CaO per 1000 mL water
1 mmol/litre	1	2	100	7,0	10,00	5,6
1 mval/litre	0,5	1	50	3,5	5,00	2,8
1 ppm	0,01	0,02	1	0,070	0,10	0,056
1 °e	0,1429	0,285	14,29	1	1,429	0,7999
1 °f	0,10	0,20	10,00	0,700	1	0,5599
1 °dH	0,1786	0,357	17,86	1,250	1,786	1
1 mg-eq/litre	2	1	50,045	3,511	5,005	2,804

5. To add a few crystals of indicator, to mix solution. It must be transparent wine-red color.
6. To add a Trilon B solution from buret to the change of solution color to sky-blue after adding of one or two last drops of titrant.
7. To calculate general hardness of water using the next formula:

$$H = N\,(\text{Trilon B})\cdot V\,(\text{Trilon B for titration of 100 mL of water})\cdot 10,$$

where H – total hardness, mg-eq/L

Results of experiment present in the form of table 21:

Table 21. Determination of total water hardness

# of titration	Normality of Trilon B solution, g-eq/L	Volume of Trilon B solution used for titration, mL	Total Hardness of water, mg-eq/L
1.	*From table 18, last column*	*Your result 1*	XX,XX
2.		*Your result 2*	
3.		*Your result 3*	

4.10. Iodometry

In acid solution practically all oxidizing agents will oxidize iodide ion to iodine quantitatively. The iodine formed in the reaction can then be titrated by means of a standard sodium thiosulfate solution. This type of indirect titration is given the general name of **iodometry.** Iodometric methods of analysis have a wide applicability for the following reasons:

1. Potassium iodide, KI, is readily available in high purity.

2. A good indicator, starch, is available to signal the equivalence point in the reaction between iodine and thiosulfate. Starch turns blue-black in the presence of iodine. Therefore, when the blue-black color disappears, the iodine has been completely reduced to the iodide ion.

3. Iodometric reactions are rapid and quantitative.

4. A precise and stable reducing agent, sodium thiosulfate ($Na_2S_2O_3$), is available to react with the iodine.

The amount of iodine liberated in the reaction between iodide ion and an oxidizing agent is a measure of the quantity of oxidizing agent originally present in the solution. The amount of standard sodium thiosulfate solution required to titrate the liberated iodine is then equivalent to the amount of oxidizing agent. Iodometric methods can be used for the quantitative determination of strong oxidizing agents such as potassium dichromate, permanganate, hydrogen peroxide, cupric ion and oxygen. As has been mentioned above, the endpoint in a titration of iodine with thiosulfate is signaled by the color change of the starch indicator. When starch is heated in water, various decomposition products are formed, among which is beta-amylose which forms a deep blue-black complex with iodine. The sensitivity of the indicator is increased by the presence of iodide ion in solution. However, if the starch indicator solution is added in the presence of a high concentration of iodine, the disappearance of the blue-black color is very gradual. For use in indirect methods, the indicator is therefore added at a point when virtually all of the iodine has been reduced to iodide ion, causing the disappearance of the color to be more rapid and sudden. The starch indicator solution must be freshly prepared since it will decompose and its sensitivity is decreased. However, a properly prepared solution will keep for a period of a few weeks. A preservative such as a small amount of mercuric ions may be added to inhibit the decomposition. Solutions of sodium thiosulfate are made up to an approximate concentration by dissolving the sodium salt in water that has previously been boiled. Boiling the water is necessary to destroy micro-organisms which metabolize the thiosulfate ion. A small amount of Na_2CO_3 is added to the solution in order to bring the pH to about 9. The solution is standardized by taking a known amount of oxidizing agent, treating it with excess iodide ion and then titrating the liberated iodine with the solution to be standardized. Oxidizing agents such as potassium dichromate, bromate, iodate or cupric ion can be employed for this procedure. You will be using potassium iodate, KIO_3, as your primary standard. The reaction between IO_3^- and I^- is given as

$$6H^+ + IO_3^- + 5I^- \text{---} > 3I_2 + 3H_2O$$

Reactions Involved in Iodometric Processes

Iodometric methods depend on the following equilibrium:

$$I_2 + I^- <===> I_3^-$$

Since the solubility of I_2 in water is quite low, the formation of the tri-iodide ion, I_3^-, allows us to obtain useful concentrations of I_2 in aqueous solutions. The equilibrium constant for this reaction is approximately 700. For this reason iodometric methods are carried out in the presence of excess iodide ion.

The reaction between iodine and the thiosulfate ion is:

$$I_2 + 2S_2O_3^{2-} <===> 2I^- + S_4O_6^{2-}$$

This reaction proceeds quantitatively in neutral or slightly acidic solutions. In strongly alkaline or acidic solutions the oxidation of the thiosulfate does not proceed by a single reaction. In the former, the thiosulfate ion is oxidized to sulfate as well as to the tetrathionate. In the latter, the thiosulfuric acid formed undergoes an internal oxidation-reduction reaction to sulfurous acid and sulfur. Both of these reactions lead to errors since the stoichiometry of the reactions differs from that shown above for the thiosulfate as a reducing agent. The control of pH is clearly important. In many cases the liberated iodine is titrated in the mildly acidic solution employed for the reaction of a strong oxidizing agent and iodide ion. In these cases the titration of the liberated iodine must be completed quickly in order to eliminate undue exposure to the atmosphere since an acid medium constitutes an optimum condition for atmospheric oxidation of the excess iodide ion. The basic reaction in the determination of copper using the iodometric method is represented by the equation:

$$2Cu^{2+} + 4I^{-} <===> 2CuI(s) + I_2$$

This is a rapid, quantitative reaction in slightly acidic solutions, if there is a large excess of iodide ion present and if the copper is in the form of a simple ion rather than a complex one. The iodine that is liberated can be titrated in the usual manner with standard thiosulfate solution. The reaction involving cupric ion and iodide takes place quantitatively since the cuprous ion formed as result of the reduction is removed from the solution as a precipitate of cuprous iodide. Iron interferes since iron (III) ions will oxidize iodide. Since the iron will be found in the +3 oxidation state as a result of the dissolution of the brass sample, a means of preventing this interference is necessary. This can be accomplished by converting the iron (III) to a soluble iron (III) phosphate complex using phosphoric acid. At a pH of 3.0-4.0 the iron phosphate complex is not reduced by iodide ion. If arsenic and antimony are present, they will provide no interference at this pH if they are in their higher oxidation states. Brass formulations also may contain up to 39% Zn, 2.5% Sn and 8.5% Pb. When dissolved in concentrated nitric acid, the zinc and the lead become Pb^{2+} and Zn^{2+}. These do not interfere with the analysis of copper because they are not reduced to the Pb^{+} and Zn^{+} states by the action of iodide ion under the conditions of this experiment. The tin is oxidized to Sn^{4+} by the concentrated nitric acid and after dilution and adjustment of pH this form becomes SnO_2 which is insoluble and may be observed as an inert white precipitate at the bottom of your flask. Under these conditions the tin does not interfere with the analysis.

The following are the most important sources of error in the iodometric method:

1. Loss of iodine by evaporation from the solution. This can be minimized by having a large excess of iodide in order to keep the iodine tied up as tri-iodide ion. It should also be apparent that the titrations involving iodine must be made in cold solutions in order to minimize loss through evaporation.

2. Atmospheric oxidation of iodide ion in acidic solution. In acid solution, prompt titration of the liberated iodine is necessary in order to prevent oxidation.

3. Starch solutions that are no longer fresh or improperly prepared. The indicator will then not behave properly at the endpoint and a quantitative determination is not possible.

4.10.1. Laboratory work. Determination of Cu in Brass

Preparation of a 0.10 M Standard $Na_2S_2O_3$ Solution

With a graduated cylinder measure out 1 liter of distilled water. Place it in your 1 liter beaker and boil the water for at least 5 minutes. Weigh out 25 g of $Na_2S_2O_3 \cdot 5H_2O$ and 0.1 g of Na_2CO_3. Dissolve the thiosulfate in the hot water and then cool this solution with the aid of an ice bath to room temperature. Then add the carbonate and stir until it is completely dissolved. Transfer the solution to your plastic 1 liter bottle. When not in use store this bottle in the darkness of your equipment cabinet as the decomposition of thiosulfate is catalyzed by light.

Blank Determination

Potassium iodide may contain appreciable amounts of iodate ion which in acid solution will react with iodide and yield iodine. The liberated iodine would react with thiosulfate and thereby cause the apparent molarity of the thiosulfate to be too low. The following procedure allows for the determination of a blank correction which will properly correct for any iodate that might be present. Prepare a solution of exactly 2.00 g of KI dissolved in 50 mL of distilled water and then acidify the solution with 5 mL of 3 M sulfuric acid and then immediately add 5 mL of starch indicator. If a blue-black color appears right after mixing, use the thiosulfate solution in the buret to determine the volume of solution required to cause the color-to disappear. This volume must be subtracted from the standardization and analyses volumes. If the potassium iodide is completely iodate-free no color will of course develop and no blank correction is necessary.

Standardization of the $Na_2S_2O_3$ Solution

Dry approximately 2 g of potassium iodate, KIO_3, at a temperature of 110 ^oC for one hour. Weigh to a precision of ±0.0001g three samples of the potassium iodate having weights near 0.12 g directly into three 250 mL Erlenmeyer flasks. Dissolve the iodate in 75 mL of distilled water. Cover the flasks with parafilm and store them. Rinse and fill your buret with the solution. Add 2.00 g of KI to each of the potassium iodate solutions. If a blank correction is required add exactly 2.00 g of KI to **each**. If no blank determination is required, the exact amount of KI is not crucial but should be close to 2 g. Then add 10 mL of 1 M HCl to one of the solutions. It will turn a dark-brown color. Immediately titrate it with the thiosulfate solution. When the color of the solution becomes very pale yellow add 5 mL of starch indicator. Continue the titration until the blue color of the starch complex just disappears. Follow the same procedure with each of the other two solutions, first adding the HCl then titrating. Correct your titration data for buret error and if necessary apply the blank correction. Calculate the molarity of the $Na_2S_2O_3$ solution. Results should agree to within 0.2% of the average. If you do not achieve that kind of precision, titrate additional samples.

Dissolution of the Brass Sample

The following procedures in this section make use of the hot plates in the fume hoods. The solutions of dissolved brass generally have a low volume and high acid and salt concentrations. "Bumping" or little explosions of steam in the superheated liquid can occur. You don't want your hand to be close to the mouth of the flask should the solution suddenly "bump" because drops of acid (not to mention part of your sample) will fly out of the flask and possibly onto your hand. For that reason you must use your tongs to place the flasks on the hot plate and to remove them. Don't use strips of paper towel or the rubber Hot Hands because your real hand will end up being too close to the mouth of the flask. The brass sample which you will receive does not have to be dried before use. Accurately weigh out three brass samples, of about 0.3 g each, directly into separate 250 mL Erlenmeyer flasks. In the fume hood add 5 mL of 6 M HNO_3. Warm the solution on a hot plate in the fume hood until dissolution is complete. Add 10 mL of concentrated (not 3 M) H_2SO_4 and continue heating until white SO_3 fumes appear. It is important that you do not mistake ordinary water vapor for SO_3 fumes. It is also important at this point that the flask ***not*** be removed from the hood. SO_3 fumes are dangerous and ought not to be inhaled. Only when the slightly denser white fumes of SO_3 are observed can you be sure that all HNO_3 has been removed. NO_3^- will oxidize I^- and hence will seriously interfere with the procedure. Cool the flask in air for one or two minutes and then in an ice bath, then carefully add 20 mL of distilled H_2O. Boil for one or two minutes then again cool in an ice bath. Continue to keep the flask in the ice bath and using your medicine dropper add concentrated $NH_3(aq)$ dropwise, and with adequate mixing, until the light-blue color of the solution is completely changed to the dark-blue color of the copper tetraammine complex. As many as 400 drops (20 mL) may be required. The solution must be kept cool in an ice bath since the reaction between the concentrated H_2SO_4 and concentrated NH_3 is highly exothermic. Now add 3 M H_2SO_4 dropwise until the dark-blue color just disappears. You don't have to produce a *complete* disappearance of the dark blue color but you need to approach that point. The subsequent addition of phosphoric acid will lower the pH appropriately to around 3.5. If you add too much 3M H_2SO_4 the pH may turn out to be sufficiently low to cause unwanted side reactions to occur when you reduce the Cu^{2+} with iodide. If you are uncertain about the disappearance of the dark blue color you may put 50 mL of 0.06 M Cu^{2+} in a clean 250 mL flask and add 12 M ammonia dropwise until you have that unmistakable dark blue color. Then add 3M H_2SO_4 dropwise until the blue color *almost* disappears. Then add 2 mL concentrated phosphoric acid and you ought to see the dark color completely disappear. You may copy that procedure to achieve an appropriate pH of around 3.5 for subsequent steps in the analysis. Now, back to your real sample: Once you are confident that you haven't added too much 3M H_2SO_4, but that you have caused the dark color of the copper tetraammine complex almost to disappear, add 2.0 mL of concentrated phosphoric acid, H_3PO_4, to each sample. Verify to yourself that they exhibit the light copper color rather than the dark color and cover the flasks with parafilm and set them aside until you are ready to proceed with the titration.

Titration of the Dissolved Brass Sample

If you have let the dissolved samples stand overnight, be sure to warm the sample on a hot plate (this can be done at your desk) in order to dissolve all larger crystals of copper sulfate that might have formed. Be sure to cool the samples to room temperature, or below, with the aid of an ice bath. The solutions will still contain a fine, white precipitate at this point; however, this will not interfere with the rest of the procedure. From this point on work with only one sample at a time. Add 4.0 g of KI to one of your samples and titrate immediately with the standard thiosulfate solution. The sample contains white CuI precipitate and the color of I_3^- must be observed against that precipitate. The slurry will at first appear brown or dark yellow-brown. Continue adding thiosulfate until the slurry is a light mustard color. At this point add 5 mL of starch indicator and titrate until the mixture in the flask takes on a milky pink or lavender hue. Now add 2 g of KSCN and mix well; the solution will darken somewhat. After the addition of thiocyanate, continue to add more thiosulfate dropwise. You should observe a sudden change to a white or cream color. That is the endpoint of the titration. After you have titrated all three samples calculate the percentage of Cu in each of the brass samples, the average percentage and the average deviation. The description above applies for brass samples with low concentrations of zinc (<10%). Some of you may have brass samples with higher concentrations of zinc. Such samples will become quite dark after the addition of KI and will lighten only slightly as thiosulfate is added. The "mustard color" will be darker than samples having low percentages of copper. When the starch is added the sample will become dark blue-black again and as you approach the end point with the thiosulfate the slurry will turn a violet color rather than milky pink or lavender hue. With the addition of the KSCN the solution will darken somewhat as in the case of the other samples, but the final end point will be a bit darker than the white or cream color described above. If you think that you have a sample with high zinc content, observe your progress carefully and take notes which will allow you to achieve repeatability.

Explanation: The reduction of Cu^{2+} to Cu^{+} occurs as the result of the oxidation of I^{-} to I_2. The I_2 combines with iodide ion to produce the dark brown triodide ion, I_3^{-}. The excess iodide ion also causes the reduced copper to precipitate as white cuprous iodide, CuI. I_2 and I_3^{-} in solution tend to adsorb on the surface of CuI thus becoming unavailable for rapid reduction by the thiosulfate. As a result, iodometric titrations involving reduced copper tend to yield lower results unless the adsorbed I_2 can be liberated by adding thiocyanate ion, SCN^{-}, which competes with the adsorbed iodine molecules on the surface of solid particles of CuI. After the addition of thiocyanate, continue to add more thiosulfate dropwise. You should observe a sudden change to a white or cream color. That is the endpoint of the titration. After you have titrated all three samples calculate the percentage of Cu in each of the brass samples, the average percentage and the average deviation.

Questions on Cu in Brass Analysis

- 1. Why is it necessary to boil the water used to prepare the thiosulfate solution?
- 2. Why is Na_2CO_3 added to the thiosulfate solution?
- 3. Why is the thiosulfate solution stored in the dark?
- 4. Why is HCl added to the IO_3^{-} mixture and why must the solution be titrated immediately?
- 5. Why is the solution containing the dissolved brass sample heated to expel SO_3 fumes?

- 6. Why is H_3PO_4 added to the brass sample?
- 7. What is the purpose of the KSCN that is added just before the endpoint in the titration?
- 8. Why is the solution containing the dissolved brass made basic with concentrated NH_3 and then again acidified with H_2SO_4?
- 9. What is the formula of the tetrammine copper (II) complex?
- 10. Why do Zn^{2+} and Pb^{2+} not interfere in this procedure?
- 11. What sort of complications would arise if the iodinethiosulfate titration were carried out in a highly acidic solution?
- 12. If the solution were highly basic, how would the iodinethiosulfate reaction be influenced?
- 13. Why is the starch indicator not added at the begin.

APPENDIXES

APPENDIX 1

MENDELEEV'S PERIODICAL TABLE OF CHEMICAL ELEMENTS

Period	**Row**	**GROUP OF ELEMENTS**			
		I	**II**	**III**	**IV**
1	**1**	**(H)**			
2	**2**	**Li 3** 6.94 **$2s^1$** **Lithium**	**Be 4** 9.01 **$2s^2$** **Beryllium**	**5 B** **$2s^2 2p^1$** 10.81 **Boron**	**6 C** **$2s^2 2p^2$** 12.01 **Carbon**
3	**3**	**Na 11** 22.99 **$3s^1$** **Sodium**	**Mg 12** 24.31 **$3s^2$** **Magnesium**	**13 Al** $3s^2 3p^1$ **26.98** **Aluminium**	**14 Si** $3s^2 3p^2$ **28.09** **Silicon**
4	**4**	**K 19** 39.10 **$4s^1$** **Potassium**	**Ca 20** 40.08 **$4s^2$** **Calcium**	**Sc 21** 44.96 **$3d^1 4s^2$** **Scandium**	**Ti 22** 47.88 **$3d^2 4s^2$** **Titanium**
	5	**29 Cu** 63.55 **$3d^{10} 4s^1$** **Copper**	**30 Zn** 65.39 **$3d^{10} 4s^2$** **Zinc**	31 Ga 69.72 **$4s^2 4p^1$** **Gallium**	**32 Ge** 72.59 **$4s^2 4p^2$** **Germanium**
5	**6**	**Rb 37** **$5s^1$** 85.47 **Rubidium**	**Sr 38** **$5s^2$** 87.62 **Strontium**	**Y 39** **$4d^1 5s^2$** 88.91 **Yttrium**	**Zr 40** **$5s^2$** 91.22 **Zirconium**
	7	**47 Ag** 107.87 **$4d^{10} 5s^1$** **Silver**	**48 Cd** 112.41 **$4d^{10} 5s^2$** **Cadmium**	**49 In** 114.82 **$5s^2 5p^1$** **Indium**	**50 Sn** 118.71 **$5s^2 5p^2$** **Tin**
6	**8**	**Cs 55** 132.91 **$4s^1$** **Cesium**	**Ba 56** 137.33 **$6s^2$** **Barium**	**La* 57** 138.91 **$5d^1 6s^2$** **Lanthanum**	**Hf 72** 178.49 **$5d^2 6s^2$** **Hafnium**
	9	**79 Au** 196.97 **$5d^{10} 6s^1$** **Gold**	**80 Hg** 200.59 **$5d^{10} 6s^2$** **Mercury**	**81 Tl** 204.38 **$6s^2 6p^1$** **Thallium**	**82 Pb** 207.2 **$6s^2 6p^2$** **Lead**
7	**10**	**Fr 87** [223] **$7s^1$** **Francium**	**Ra 38** 226.03 **$7s^2$** **Radium**	**Ac** 89** 227.03 **$6d^1 7s^2$** **Actinium**	**Unq 104** [261] **$6d^2 7s^2$** **Unnilquadium**

LANTANIDES						
Ce 58 140.12 **Cerium**	**Pr 59** 140.908 **Praseodymium**	**Nd 60** 144.24 **Neodymium**	**Pm 61** [145] **Promethium**	**Sm 62** 150.36 **Samarium**	**Eu 63** 151.96 **Europium**	**Gd 64** 157.25 **Gadolinium**
ACTINIDES						
Th 90 232.038 **Thorium**	**Pa 91** 231.036 **Protactinium**	**U 92** 238.029 **Uranum**	**Np 93** 237.048 **Neptunium**	**Np 94** [244] **Plutonium**	**Am 95** [243] **Americium**	**Cm 96** [247] **Curium**

CONTINIED APPENDIX 1

GROUP OF ELEMENTS					
V	VI	VII	VIII		
		1 H 1.01 $1s^1$ **Hydrogen**	**2 He** 4.00 $2s^1$ **Helium**		
7 N 14.01 $2s^22p^3$ **Nitrogen**	**8 O** 16.00 $2s^22p^4$ **Oxygen**	**9 F** 19.00 $2s^22p^5$ **Fluorine**	**10 Ne** 20.18 $2s^22p^6$ **Neon**		
15 P 30.97 $3s^23p^3$ **Posphorus**	**16 S** 32.06 $3s^23p^4$ **Sulfur**	**17 Cl** 35.45 $3s^23p^5$ **Chlorine**	**18 Ar** 39.95 $3s^23p^6$ **Argon**		
V 23 $3d^34s^2$ 50.94 **Vanadium**	**Cr 24** $3d^54s^1$ 52.00 **Chromium**	**Mn 25** $3d^54s^2$ 54.94 **Manganese**	**Fe 26** $3d^64s^2$ 55.85 **Iron**	**Co 26** $3d^74s^2$ 58.93 **Cobalt**	**Ni 27** $3d^84s^2$ 58.69 **Nickel**
33 As 74.92 $4s^24p^3$ **Arsenic**	34 **Se** 78.96 $4s^24p^4$ **Selenium**	**35 Br** 79.90 $4s^24p^5$ **Bromine**	36 **Kr** 83.80 $4s^2\ 4p^6$ **Krypton**		
Nd 41 $4d^45s^1$ 92.91 **Niobium**	**Mo 42** 95.94 $4d^55s^1$ **Molybdenum**	**Tc 43** 98.91 $4d^55s^2$ **Technetium**	**Ru 44** 101.07 $4d^75s^1$ **Ruthenium**	**Rh 45** 102.9 $4d^85s^1$ **Rhodium**	**Pd 46** 106.4$4d^{10}5s^0$ **Palladium**
51 Sb 121.75 $5s^25p^3$ **Antimony**	**52 Te** 127.60 $5s^25p^4$ **Tellurium**	**53 I** 126.91 $5s^25p^5$ **Iodine**	**54 Xe** 131.29 $5s^2\ 5p^6$ **Xenon**		
Ta 73 180.95 $5d^36s^2$ **Tantalum**	**W 74** 183.85 $5d^46s^2$ **Tungsten**	**Re 75** 186.21 $5d^56s^2$ **Rhenium**	**Os 76** 190.2 $5d^66s^2$ **Osmium**	**Ir 77** 192.22 $5d^76s^2$ **Iriudium**	**Pt 78** 195.1 $5d^96s^1$ **Platinum**
83 Bi 208.98 $6s^26p^3$ **Bismuth**	**84 Po** [209] $6s^26p^4$ **Polonium**	**85 At** [210] $6s^26p^5$ **Astatine**	**86 Rn** [222] $6s^26p^6$ **Radon**		
Unp 105 [262] $6d^37s^2$ **Unnilpentium**	**Unh 106** [263**]** $6d^47s^2$ **Unnilhexium**	**Uns 107** [262] $6d^57s^2$ **Unnilseptium**	**Uno 108** [265] $6d^67s^2$ **Unniloctium**	**Une 109** [266?] $6d^77s^2$ **Unnilennium**	

Tb 65 158.93 **Terbium**	**Dy 66** 162.50 **Dysprosium**	**Ho 67** 164.93 **Holmium**	**Er 68** 167.26 **Erbium**	**Tm 69** 168.934 **Thulium**	**Yb 70** 173.04 **Ytterbium**	**Lu 71** 174.967 **Lutetium**

Bk 97 [247] **Berkelium**	**Cf 98** [251] **Californium**	**Es 99** [252] **Einsteinium**	**Fm 100** [257] **Fermium**	**Md 101** [258] **Mendelevium**	**No 102** [259] **Nobelium**	**Lr 103** [260] **Lawrencium**

APPENDIX 2

Solubility of salts and bases in water

Anions	**Cations**											
	K^+	**Na^+**	**NH_4^+**	**Ba^{2+}**	**Sr^{2+}**	**Ca^{2+}**	**Mg^{2+}**	**Al^{3+}**	**Cr^{3+}**	**Fe^{3+}**	**Fe^{2+}**	**Mn^{2+}**
OH^-	S	S	S	S	S	SS	S	I	I	I	I	I
F^-	S	S	S	SS	SS	SS	SS	SS	SS	SS	SS	SS
Cl^-	S	S	S	S	S	S	S	S	S	S	S	S
Br^-	S	S	S	S	S	S	S	S	S	S	S	S
I^-	S	S	S	S	S	S	S	S	S	S	S	S
S^{2-}	S	S	S	S	SS	S	SS	-	-	I	I	I
SO_3^{2-}	S	S	S	I	I	I	SS	-	-	-	I	-
SO_4^{2-}	S	S	S	I	SS	SS	S	S	S	S	S	S
PO_4^{3-}	S	S	S	I	I	I	I	I	SS	I	I	I
CrO_4^{2-}	S	S	S	I	SS	S	S	-	-	-	-	I
CO_3^{2-}	S	S	S	I	I	I	I	-	-	-	I	I
NO_3^-	S	S	S	S	S	S	I	S	S	S	S	S
NO_2^-	S	S	S	S	S	S	S	S	S	S	S	S
CH_3COO^-	S	S	S	S	S	S	S	S	S	S	S	S

Notes: S – soluble in water; SS – slightly soluble; I – practically insoluble; dash line (-) – substance decomposed in water

CONTINIED APPENDIX 2

Anions	**Cations**									
	Zn^{2+}	**Ni^{2+}**	**Co^{2+}**	**Ag^{+}**	**Hg^{2+}**	**Cu^{2+}**	**Cd^{2+}**	**Pb^{2+}**	**Bi^{3+}**	**Sn^{2+}**
OH^-	I	I	I	SS	I	I	I	I	I	I
F^-	SS	S	S	S	-	SS	SS	I	I	S
Cl^-	S	S	S	I	S	S	S	SS	-	S
Br^-	S	S	S	I	S	S	S	SS	-	S
I^-	S	S	S	I	I	I	S	SS	I	S
S^{2-}	I	I	I	I	I	I	I	I	I	I
SO_3^{2-}	I	I	-	I	-	-	I	I	-	-
SO_4^{2-}	S	S	S	SS	-	S	S	I	S	S
PO_4^{3-}	I	I	I	I	I	I	I	I	I	-
CrO_4^{2-}	I	I	I	I	I	I	I	I	I	I
CO_3^{2-}	I	I	I	I	I	I	I	I	I	-
NO_3^-	S	S	S	S	S	S	S	S	S	-
NO_2^-	S	S	S	SS	-	S	S	S	S	-
CH_3COO^-	S	S	S	SS	S	S	S	S	-	-

Notes: S – soluble in water; SS – slightly soluble; I – practically insoluble; dash line (-) – substance decomposed in water

APPENDIX 3

Density of water solutions of the bases (18 ^{0}C), g/cm^3

%	KOH	NaOH	NH_3
4	1,033	1,046	0,983
6	1,048	1,069	0,973
8	1,065	1,092	0,967
10	1,082	1,115	0,960
12	1,100	1,137	0,958
14	1,118	1,159	0,946
16	1,137	1,181	0,939
18	1,156	1,203	0,932
20	1,176	1,225	0,926
22	1,196	1,247	0,919
24	1,217	1,268	0,913
26	1,240	1,289	0,908
28	1,263	1,310	0,903
30	1,286	1,332	0,898
32	1,310	1,352	0,893
34	1,334	1,374	0,889
36	1,358	1,395	0,884
38	1,384	1,416	-
40	1,411	1,437	-
42	1,437	1,458	-
44	1,460	1,478	-
46	1,485	1,499	-
48	1,511	1,519	-
50	1,538	1,540	-
52	1,564	1,560	-
54	1,590	1,580	-
56	1,616	1,601	-
58	-	1,622	-
60	-	1,643	-

APPENDIX 4

Density of water solutions of the acids (18^{0}C), g/cm^3

%	H_2SO_4	HNO_3	HCl		%	H_2SO_4	HNO_3	HCl
4	1,027	1,020	1,018		**52**	1,415	1,322	-
6	1,038	1,031	1,028		**54**	1,435	1,334	-
8	1,052	1,043	1,038		**56**	1,456	1,345	-
10	1,066	1,054	1,047		**58**	1,477	1,356	-
12	1,080	1,066	1,057		**60**	1,498	1,367	-
14	1,095	1,078	1,068		**62**	1,520	1,377	-
16	1,109	1,090	1,078		**64**	1,542	1,387	-
18	1,124	1,103	1,088		**66**	1,565	1,396	-
20	1,139	1,115	1,098		**68**	1,587	1,405	-
22	1,155	1,128	1,108		**70**	1,611	1,413	-
24	1,170	1,140	1,119		**72**	1,634	1,422	-
26	1,176	1,153	1,129		**74**	1,657	1,430	-
28	1,202	1,167	1,139		**76**	1,681	1,438	-
30	1,219	1,180	1,149		**78**	1,704	1,445	-
32	1,235	1,193	1,159		**80**	1,727	1,452	-
34	1,252	1,207	1,169		**82**	1,749	1,459	-
36	1,268	1,221	1,179		**84**	1,769	1,466	-
38	1,286	1,234	1,189		**86**	1,787	1,372	-
40	1,303	1,246	1,198		**88**	1,802	1,477	-
42	1,,321	1,259	-		**90**	1,814	1,483	-
44	1,338	1,272	-		**92**	1,824	1,487	-
46	1,357	1,285	-		**94**	1,8312	1,491	-
48	1,376	1,298	-		**96**	1,8355	1,495	-
50	1,395	1,310	-		**98**	1,8395	1,501	-
					100	1,8305	1,513	-

APPENDIX 5

Analytical Standards

Standards are materials containing a known concentration of an analyte. They provide a reference to determine unknown concentrations or to calibrate analytical instruments.

The accuracy of an analytical measurement is how close a result comes to the true value. Determining the accuracy of a measurement usually requires calibration of the analytical method with a known standard. This is often done with standards of several concentrations to make a calibration or working curve.

Primary Standards

A primary standard is a reagent that is extremely pure, stable, has no waters of hydration, and has a high molecular weight.

Some primary standards for titration of acids:

sodium carbonate: Na_2CO_3, mol wt. = 105.99 g/mol

- *tris*-(hydroxymethyl)aminomethane (TRIS or THAM): $(CH_2OH)_3CNH_2$, mol wt. = 121.14 g/mol

Some primary standards for titration of bases:

- potassium hydrogen phthalate (KHP): $KHC_8H_4O_4$, mol wt. = 204.23 g/mol
- potassium hydrogen iodate: $KH(IO_3)_2$, mol wt. = 389.92 g/mol

Some primary standards for redox titrations:

- potassium dichromate: $K_2Cr_2O_7$, mol wt. = 294.19 g/mol

Secondary Standards

A secondary standard is a standard that is prepared in the laboratory for a specific analysis. It is usually standardized against a primary standard.

APPENDIX 6

Standard electrode potentials (as reduction potentials)

Element	**The highest oxidation number**	**Quantity of electrons**	**The lowest oxidation number**	**E^0 (in Volts)**
1	2	3	4	5
Ag	Ag^+	$+ e^-$	$Ag\downarrow$	+ 0,7994
	$Ag(NH_3)_2^+$	$+ e^-$	$Ag\downarrow + 2\ NH_3$	+ 0,373
Al	Al^{3+}	$+ 3\ e^-$	$Al\downarrow$	- 0,66
Ba	Ba^{2+}	$+ 2\ e^-$	$Ba\downarrow$	- 2,91
Be	Be^{2+}	$+ 2\ e^-$	$Be\downarrow$	- 1,97
Br	Br_2	$+ 2\ e^-$	$2Br^-$	+ 1,087
	$2HBrO + 2\ H^+$	$+ 2\ e^-$	$Br_2\uparrow + 2\ H_2O$	+ 1,6
	$2BrO^- + 2\ H_2O$	$+ 2\ e^-$	$Br_2\uparrow + 4\ OH^-$	+ 0,45
	$HBrO + H^+$	$+ 2\ e^-$	$Br^- + H_2O$	+ 1,34
	$BrO^- + H_2O$	$+ 2\ e^-$	$Br^- + 2OH^-$	+ 0,76
	$BrO_3^- + 5\ H^+$	$+ 4\ e^-$	$HBrO + 2H_2O$	+ 1,45
	$BrO_3^- + 2\ H_2O$	$+ 4\ e^-$	$BrO^- + 4OH^-$	+ 0,54
	$2BrO_3^- + 12\ H^+$	$+ 10\ e^-$	$Br_2\uparrow + 6H_2O$	+ 1,52
	$BrO_3^- + 6\ H^+$	$+ 6\ e^-$	$Br^- + 6H_2O$	+ 1,45
Ca	Ca^{2+}	$+ 2\ e^-$	$Ca\downarrow$	- 2,79
Cd	Cd^{2+}	$+ 2\ e^-$	$Cd\downarrow$	- 0,403

1	2	3	4	5
Cl	Cl_2	$+ 2 e^-$	$2Cl^-$	+ 1,359
	$2HOCl + 2 H^+$	$+ 2 e^-$	$Cl_2\uparrow + 4H_2O$	+ 1,63
	$HClO + H^+$	$+ 2 e^-$	$Cl^- + H_2O$	+ 1,50
	$2HClO_2 + 6 H^+$	$+ 6 e^-$	$Cl_2\uparrow + 4H_2O$	+ 1,63
	$HClO_2 + 3 H^+$	$+ 4 e^-$	$Cl^- + 4H_2O$	+ 1,63
	$ClO_3^- + 6 H^+$	$+ 6 e^-$	$Cl^- + 6 OH^-$	+ 0,63
	$ClO_4^- + 2 H^+$	$+ 2 e^-$	$ClO_3^- + H_2O$	+ 1,19
	$2 ClO_4^- + 16 H^+$	$+14 e^-$	$Cl_2\uparrow + 8 H_2O$	+ 1,39
	$ClO_4^- + 4 H_2O$	$+ 8 e^-$	$Cl^- + 8 OH^-$	+ 0,56
Co	Co^{3+}	$+ e^-$	Co^{2+}	+ 1,95
	Co^{3+}	$+ 3 e^-$	$Co\downarrow$	+ 0,46
	Co^{2+}	$+ 2 e^-$	$Co\downarrow$	- 0,29
Cr	Cr^{3+}	$+ e^-$	Cr^{2+}	- 0,41
	Cr^{3+}	$+ 3 e^-$	$Cr\downarrow$	- 0,74
	Cr^{2+}	$+ 2 e^-$	$Cr\downarrow$	- 0,91
	$CrO_2^- + 2 H_2O$	$+ 3 e^-$	$Cr\downarrow + 4 OH^-$	- 1,2
	$Cr_2O_7^{2-} + 14 H^+$	$+ 6 e^-$	$2 Cr^{3+} + 7 H_2O$	+ 1,33
	$CrO_4^{2-} + 4 H_2O$	$+ 3 e^-$	$Cr(OH)_3\downarrow + 5 OH^-$	- 0,13
Cs	Cs^+	$+ e^-$	$Cs\downarrow$	- 2,923
Cu	Cu^{2+}	$+ e^-$	Cu^+	+ 0,159
	Cu^{2+}	$+ 2 e^-$	$Cu\downarrow$	+ 0,345
	Cu^+	$+ e^-$	$Cu\downarrow$	+ 0,531
	$Cu^{2+} + I^-$	$+ e^-$	$CuI\downarrow$	+ 0,86

1	2	3	4	5
F	$F_2\uparrow$	$+ 2 e^-$	$2 F^-$	+ 2,77
Fe	Fe^{3+}	$+ e^-$	Fe^{2+}	+ 0,771
	Fe^{3+}	$+ 3 e^-$	$Fe\downarrow$	- 0,058
	Fe^{2+}	$+ 2 e^-$	$Fe\downarrow$	- 0,473
Fe	$FeO_4^{2-} + 8 H^+$	$+ 3 e^-$	$Fe^{3+} + 4 H_2O$	+ 1,9
Ga	Ga^{3+}	$+ 3 e^-$	$Ga\downarrow$	- 0,56
Ge	Ge^{2+}	$+ 2 e^-$	$Ge\downarrow$	0,0
H	$2 H^+$	$+ 2 e^-$	$H_2\uparrow$	0,0000
	$2 H_2O$	$+ 2 e^-$	$H_2\uparrow + 2 OH^-$	- 0,828
Hf	$HfO^{2+} + 2 H^+$	$+ 4 e^-$	$Hf\downarrow + H_2O$	- 1,70
Hg	$2 Hg^{2+}$	$+ 2 e^-$	Hg_2^{2+}	+ 0,907
	Hg^{2+}	$+ 2 e^-$	$Hg\downarrow$	+ 0,850
	$2 Hg^{2+}$	$+ 2 e^-$	2 Hg	+ 0,792
I	I_2	$+ 2 e^-$	$2 I^-$	+ 0,621
	I_3^-	$+ 2 e^-$	$3 I^-$	+0,546
	2 IBr	$+ 2 e^-$	$I_2\downarrow + 2 Br^-$	+ 1,02
	2 ICl	$+ 2 e^-$	$I_2\downarrow + 2 Cl^-$	+ 1,19
	$2 HIO + 2 H^+$	$+ 2 e^-$	$I_2\downarrow + 2 H_2O$	+ 1,45
	$2 IO^- + 2 H_2O$	$+ 2 e^-$	$I_2\downarrow + 4 OH^-$	+ 0,45
	$HIO + H^+$	$+ 2 e^-$	$I^- + H_2O$	+ 0,99
	$IO^- + H_2O$	$+ 2 e^-$	$I^- + 2 OH^-$	+ 0,49
	$IO_3^- + 5 H^+$	$+ 4 e^-$	$HIO + 2 H_2O$	+ 1,14
	$IO_3^- + 2 H_2O$	$+ 4 e^-$	$IO^- + 4 OH^-$	+ 0,14

1	2	3	4	5
I	$2\ IO_3^- + 12\ H^+$	$+ 10\ e^-$	$I_2\downarrow + 6\ H_2O$	+ 1,19
	$2\ IO_3^- + 6\ H_2O$	$+ 10\ e^-$	$I_2\downarrow + 12\ OH^-$	+ 0,21
	$IO_3^- + 6\ H^+$	$+ 6\ e^-$	$I^- + 3\ H_2O$	+ 1,08
In	$IO_3^- + 3\ H_2O$	$+ 6\ e^-$	$I^- + 6\ OH^-$	+ 0,26
	$H_5IO_6 + H^+$	$+ 2\ e^-$	$IO_3^- + 3\ H_2O$	+ 1,6
Ir	$H_3IO_6^{2-}$	$+ 2\ e^-$	$IO_3^- + 3\ OH^-$	+ 0,7
K	K^+	$+ e^-$	$K\downarrow$	- 2,923
Li	Li^+	$+ e^-$	$Li\downarrow$	- 3,04
Mg	Mg^{2+}	$+ 2\ e^-$	$Mg\downarrow$	- 2,37
Mn	Mn^{3+}	$+ e^-$	Mn^{2+}	+ 1,51
	Mn^{2+}	$+ 2\ e^-$	$Mn\downarrow$	- 1,17
	$MnO_4^{2-} + 4\ H^+$	$+ 2\ e^-$	$MnO_2\downarrow + 2\ H_2O$	+ 2,26
	$MnO_4^{2-} + 2\ H_2O$	$+ 2\ e^-$	$MnO_2\downarrow + 4\ OH^-$	+ 0,6
	MnO_4^-	$+ e^-$	MnO_4^{2-}	+ 0,588
	$MnO_4^- + 4\ H^+$	$+ 3\ e^-$	$MnO_2\downarrow + 2\ H_2O$	+ 1,69
	$MnO_4^- + 8\ H^+$	$+ 5\ e^-$	$Mn^{2+} + 4\ H_2O$	+ 1,51
Mo	Mo^{3+}	$+ 3\ e^-$	$Mo\downarrow$	- 0,2
	$MoO_2^+ + 4\ H^+$	$+ 2\ e^-$	$Mo^{3+} + 2\ H_2O$	0,0
	$H_2MoO_4 + 6\ H^+$	$+ 6\ e^-$	$Mo\downarrow + 4\ H_2O$	+ 0,48
	$MoO_4^{2-} + 4\ H_2O$	$+ 6\ e^-$	$Mo\downarrow + 8\ OH^-$	-1,05
N	$NH_3 + 11\ H^+$	$+ 8\ e^-$	$3\ NH_4^+$	+ 0,69
	$N_3^- + 7\ H_2O$	$+ 6\ e^-$	$N_2H_4 + NH_3 + 7\ OH^-$	- 0,62
	$3\ N_2\uparrow + 2\ H^+$	$+ 2\ e^-$	$2\ NH_3$	- 3,1

1	2	3	4	5
N	$3\,N_2\uparrow$	$+ 2\,e^-$	$2\,N_3^-$	- 3,4
	$N_2\uparrow + 8\,H^+$	$+ 6\,e^-$	$2\,NH_4^+$	+ 0,26
	$HNO_2 + H^+$	$+ e^-$	$NO\uparrow + H_2O$	+ 0,98
	$NO_2^- + H_2O$	$+ e^-$	$NO\uparrow + 2\,OH^-$	- 0,46
	$2\,HNO_2 + 4\,H^+$	$+ 4\,e^-$	$N_2O\uparrow + 3\,H_2O$	+ 1,29
	$2\,HNO_2 + 6\,H^+$	$+ 6\,e^-$	$N_2\uparrow + 4\,H_2O$	+ 1,44
	$2\,NO_2^- + 4\,H_2O$	$+ 6\,e^-$	$N_2\uparrow + 8\,OH^-$	+ 0,41
	$HNO_2 + 7\,H^+$	$+ 6\,e^-$	$NH_4^+ + 2\,H_2O$	+ 0,86
	$NO_2^- + 6\,H_2O$	$+ 6\,e^-$	$NH_4OH + 7\,OH^-$	- 0,15
	$N_2O\uparrow + 2\,H^+$	$+ 2\,e^-$	$N_2\uparrow + H_2O$	+ 1,77
	$N_2O\uparrow + H_2O$	$+ 2\,e^-$	$N_2\uparrow + 2\,OH^-$	+ 0,94
	$NO_3^- + 4\,H^+$	$+ 3\,e^-$	$NO\uparrow + 2\,H_2O$	+ 0,96
	$NO_3^- + 2\,H_2O$	$+ 3\,e^-$	$NO\uparrow + 4\,OH^-$	- 0,14
	$NO_3^- + 12\,H^+$	$+10\,e^-$	$N_2\uparrow + 6\,H_2O$	+ 0,73
	$NO_3^- + 8\,H^+$	$+ 6\,e^-$	$NH_3OH^+ + 2\,H_2O$	+ 0,73
	$NO_3^- + 17\,H^+$	$+ 14\,e^-$	$N_2H_5^+ + 6\,H_2O$	+ 0,84
	$NO_3^- + 10\,H^+$	$+ 8\,e^-$	$NH_4^+ + 3\,H_2O$	+ 0,87
	$NO_3^- + 7\,H_2O$	$+ 8\,e^-$	$NH_4OH + 9\,OH^-$	- 0,12
Na	Na^+	$+ e^-$	$Na\downarrow$	- 2,713
Ni	Ni^{2+}	$+ 2\,e^-$	$Ni\downarrow$	- 0,228
O	$O_2\uparrow + 4\,H^+$	$+ 4\,e^-$	$2\,H_2O$	+ 1,229
	$O_2\uparrow + 2\,H_2O$	$+ 4\,e^-$	$4\,OH^-$	+ 0,401
	$O_2\uparrow + 2\,H^+$	$+ 2\,e^-$	H_2O_2	+ 0,682

1	2	3	4	5
O	$O_2\uparrow + H_2O$	$+ 2 e^-$	$HO_2^- + OH^-$	- 0,076
	$H_2O_2 + 2 H^+$	$+ 2 e^-$	$2 H_2O$	+ 1,77
	$HO_2^- + H_2O$	$+ 2 e^-$	$3 OH^-$	+ 0,88
	$O_3\uparrow + 2 H^+$	$+ 2 e^-$	$O_2\uparrow + H_2O$	+ 2,07
	$O_3\uparrow + H_2O$	$+ 2 e^-$	$O_2\uparrow + 2 OH^-$	+ 1,24
P	$H_3PO_2 + H^+$	$+ e^-$	$P\downarrow + 2 H_2O$	- 0,51
	$H_3PO_3 + 3 H^+$	$+ 3 e^-$	$P\downarrow + 3 H_2O$	- 0,50
	$H_3PO_4 + 5 H^+$	$+ 5 e^-$	$P\downarrow + 4 H_2O$	- 0,41
	$H_3PO_4 + 2 H^+$	$+ 2 e^-$	$H_3PO_3 + H_2O$	- 0,276
	$PO_4^{3-} + 2 H_2O$	$+ 2 e^-$	$HPO_3^{2-} + 3 OH^-$	- 1,12
Pb	Pb^{4+}	$+ 2 e^-$	Pb^{2+}	+ 1,66
	Pb^{4+}	$+ 4 e^-$	$Pb\downarrow$	+ 0,77
	Pb^{2+}	$+ 2 e^-$	$Pb\downarrow$	- 1,26
	$HPbO_2^- + H_2O$	$+ 2 e^-$	$Pb\downarrow + 3 OH^-$	- 0,54
	$PbO_3^{2-} + H_2O$	$+ 2 e^-$	$PbO_2^{2-} + 2 OH^-$	+ 0,2
Pt	Pt^{2+}	$+ 2 e^-$	$Pt\downarrow$	+ 1,2
Rb	Rb^+	$+ e^-$	$Rb\downarrow$	- 2,924
S	$S_2O_3^{2-} + 6 H^+$	$+ 4 e^-$	$2 S\downarrow + 3 H_2O$	+ 0,5
	$2 H_2SO_3 + 2 H^+$	$+ 4 e^-$	$S_2O_3^{2-} + 3 H_2O$	+ 0,40
	$SO_3^{2-} + 3 H_2O$	$+ 4 e^-$	$S_2O_3^{2-} + 6 OH^-$	- 0,58
	$2 H_2SO_3 + H^+$	$+ 2 e^-$	$HS_2O_4^- + 2 H_2O$	- 0,08
	$2 SO_3^{2-} + 2 H_2O$	$+ 2 e^-$	$S_2O_4^{2-} + 4 OH^-$	- 1,12
	$SO_4^{2-} + 4 H^+$	$+ 2 e^-$	$H_2SO_3 + H_2O$	+ 0,17

APPENDIX 7

Some Familiar Substances with their systematic and common names

Chemical Formula	**Systematic Name**	**Common name**
1	2	3
Alloy: 1 part of $AgNO_3$ with 2 part of KNO_3	-	Lunar caustic
$AlF_3 \cdot NaF$	-	Cryolite
$Al_2O_3 \cdot 2\ SiO_2 \cdot 2\ H_2O$	-	Kaolin (mineral)
As_2O_5	Arsenic (V) oxide	Arsenic Anhydride
$Ba(OH)_2$ (aqueous solution)	Barium Hydroxide	Barytic Water
$BaSO_4$	Barium Sulfate	Heavy Spar
CaF_2	Calcium fluoride	Fluor-Spar (mineral)
$Ca(NO_3)_2$	Calcium Nitrate	Calcium Saltpeter
CO	Carbon (II) oxide	Full of coal gas
CO_2	Carbon dioxide	Dry Ice (solid CO_2)
CH_3OH	Methanol	Wood Alcohol
C_2H_5OH	Ethanol	Grain Alcohol
$CaCO_3$	Calcium Carbonate	Limestone, Calcite, Marble
$Ca(H_2PO_4)_2 \cdot H_2O$	-	Simple SuperPhosphate
$Ca(H_2PO_4)_2 \cdot H_2O + 2[CaSO_4 \cdot 2H_2O]$	-	Triple SuperPhosphate
$CaHPO_4 \cdot 2H_2O$	Calcium Hydrophospate Dihydrate	Precipitate
CaO	Calcium Oxide	Lime
$Ca(OH)_2$	Calcium Hydroxide	Slaked/slack Lime
$Ca(OH)_2$ (aq)	Calcium Hydroxide (water solution)	Limewater, Lime Milk
2CaO + NaOH	Mixture of Calcium Oxide and Sodium Hydroxide	Soda Lime
$CaOCl_2$	Calcium Hypochlorite-Chloride	Chloride of Lime, Bleaching Powder
$3Ca_3(PO_4)_2 \cdot Ca(F, Cl)_2$	-	Apatite (mineral)
$CaSO_4 \cdot 1/2\ H_2O$	Calcium Sulfate Hemihydrate	Plaster of Paris, alabaster

1	2	3
$CaSO_4 \cdot 2\ H_2O$	Alcium Sulfate Dihydrate	Gypsum
$Cu(CH_3COO)_2x$ $3\ Cu(AsO_2)_2$	Mixed salt - Copper Acetate-arsenite	Paris Green
$2\ CuCO_3 \cdot Cu(OH)_2$ $CuCO_3 \cdot Cu(OH)_2$	Mixed Copper Hydroxide-Carbonate	Azurite (mineral) Malachite (mineral)
$CuSO_4 \cdot 5\ H_2O$	Copper (II) Sulfate Pentahydrate	Blue Vitriol
$Fe_3[Fe(CN)_6]_2$	Iron (II) Hexacianoferrate (III)	Turnbull’s Blue
$Fe_4[Fe(CN)_6]_3$	Iron (III) Hexacianoferrate (II)	Prussian Blue
Fe_2O_3	Iron (III) Oxide	Mummy (mineral colour)
Fe_3O_4 or $FeO \cdot Fe_2O_3$	Mixed Iron (II) and Iron (III) Oxide	Loadstone, Magnetite (mineral)
FeS_2	Iron (II) PerSulfide	Pyrite, Brazil; Fool's Gold, Sulfur-Ore (mineral)
$FeSO_4 \cdot 7\ H_2O$	Iron (II) Sulfate Heptahydrate	Green Vitriol
HCl	Hydrochloric acid	Muriatic Acid
HF	Hydrofluoric	Etching Acid
H_2O_2 (27-31% solution)	Hydrogen Peroxide	Perhydrol
H_2SO_4 (90,5 – 92,5%)	Concentrated Sulfuric Acid	Vitriolic Oil
Hg	Mercury	Quicksilver
HgS	Mercury (II) Sulfide	Cinnabar, Vermilion (mineral)
Hg_2Cl_2	Mercury (I) Chloride	Calomel
$HgCl_2$	Mercury (II) Chloride	(Corrosive) Sublimate
$KAl(SO_4)_2 \cdot 12\ H_2O$	Potassium-Aluminium Sulfate	Potash Alum
$KCl \cdot MgCl_2 \cdot 6H_2O$	Potassium-Magnesium hexahydrate	Carnallite (mineral)
KNO_3	Potassium Nitrate	Caliche (Indian Saltpetre)

1	2	3
KOH	Potassium Hydroxide	Caustic Potash, Potassa
$K_4[Fe(CN_6)]$ $K_3[Fe(CN)_6]$	Potassium Hexacianoferrate (II) Potassium Hexacianoferrate (III)	Yellow blood salt Red blood salt
K_2CO_3	Potassium Carbonate	Potash
$KNaC_4H_4O_6$	Potassium-Sodium Hydrotartrate	Rochelle Salt
$MgCO_3$	Magnesium Carbonate	Magnesite (mineral)
MgO	Magnesium Oxide	Magnesia Alba
$3\ MgO\cdot 4\ SiO_2\cdot H_2O$	-	Talc (mineral)
$Mg(OH)_2$	Magnesium Hydroxide	Milk of Magnesia
$MgSO_4\cdot 7H_2O$	Magnesium Sulfate Heptahydrate	Epsom Salt
Mixture of conc, HNO_3 (1 volume) and conc, HCl (3 volumes)	-	Aqua-regia
Mixture of solution $CuSO_4$ with $Ca(OH)_2$	-	Bordeaux Mixture
$MnO_2\cdot nH_2O$	Manganese (IV) Oxide Hydrate	Pyrolusite Black (mineral)
NH_4Cl	Ammonia Chloride (solution)	Sal Ammoniac
NH_4NO_3	Ammonium Nitrate	Ammonium Nitre
NH_4OH	Ammonium Hydroxide	Ammonia Water, Aueous/liquid Ammonia
N_2O	Nitrogen (I) oxide	Laughing Gas
$Na_2CO_3\cdot 10H_2O$	Sodium CarbonateDecahydrate	Washing Soda
NaCl	Sodium Chloride	Table salt, White salt
$NaHCO_3$	Sodium HydroCarbonate	Baking Soda
$NaNO_3$	Sodium Nitrate	Chile Saltpetre
NaOH	Sodium Hydroxide	Lye, Caustic Soda

1	2	3
$Na_3PO_4 \cdot 10H_2O$	Sodium Phospate Decahydrate	TSP
$Na_2S_2O_3$ or $Na_2S_2O_3 \cdot 5H_2O$	Sodium Thiosulfate or Sodium Thiosulfate Pentahydrate	Antichlor
$Na_2B_4O_7 \cdot 10\ H_2O$	Sodium Tetraborate Decahydrate	Borax
$Na_2SO_4 \cdot 10\ H_2O$	Sodium Sulfate Decahydrate	Glauber's Salt
P_2O_5 or P_4O_{10}	Phosphorus (V) Oxide	Phosphoric Anhydride
$2PbCO_3 \cdot Pb(OH)_2$	Lead (II) Carbonate-Hydroxide-	White Lead
$Pb(CH_3COO)_2 \cdot 3H_2O$	Lead (II) Acetate Trihydrate	Lead Sugar
PbO	Lead (II) Oxide	Litharge
PbS	Lead (II) Sulphide	Galena, Lead Glance (mineral)
S	Sulfur (Sulfur)	Brimstone
SO_3	Sulfur (VI) Oxide	Sulfuric Anhydride
SiO_2	Silicon (IV) Oxide	Quartz, Sand
Solution of (15,5-60%) SO_3 in H_2SO_4	-	Oleum
TiO_2	Titanium (IV) Oxide	Titanium White
$ZnSO_4 \cdot 7\ H_2O$	Zinc (II) Sulfate Heptahydrate	Zinc Vitriol
ZnO	Zinc Oxide	Zinc White

APPENDIX 8

Ionization constants of some acids and bases (25^{0}C)

Compound	Expression for ionization constant	$К_{ionization}$	pК = - lg $К_{dis}$
1	2	3	4
HF	$K = \frac{[H^+][F^-]}{[HF]}$	$6{,}8 \cdot 10^{-4}$	3,20
HCl	$K = \frac{[H^+][Cl^-]}{[HCl]}$	$1{,}0 \cdot 10^{7}$	-7,00
HBr	$K = \frac{[H^+][Br^-]}{[HBr]}$	$1{,}0 \cdot 10^{9}$	-9,00
HI	$K = \frac{[H^+][I^-]}{[HI]}$	$1{,}0 \cdot 10^{11}$	-11,00
HClO	$K = \frac{[H^+][ClO^-]}{[HClO]}$	$3{,}0 \cdot 10^{-8}$	7,53
$HClO_2$	$K = \frac{[H^+][ClO_2^-]}{[HClO_2]}$	$1{,}1 \cdot 10^{-2}$	1,97
HBrO	$K = \frac{[H^+][BrO^-]}{[HBrO]}$	$2{,}5 \cdot 10^{-9}$	8,66
HIO	$K = \frac{[H^+][IO^-]}{[HIO]}$	$2{,}3 \cdot 10^{-11}$	10,64
HIO_3	$K = \frac{[H^+][IO_3^-]}{[HIO_3]}$	$1{,}6 \cdot 10^{-11}$	10,80
H_2S	$K_1 = \frac{[H^+][HS^-]}{[H_2S]}$ $K_2 = \frac{[H^+][S^{2-}]}{[HS^-]}$	$1{,}0 \cdot 10^{-7}$ $2{,}5 \cdot 10^{-18}$	6,99 12,60
H_2SO_3	$K_1 = \frac{[H^+][HSO_3^-]}{[H_2SO_3]}$ $K_2 = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]}$	$1{,}4 \cdot 10^{-2}$ $6{,}2 \cdot 10^{-8}$	1,85 7,20
H_2SO_4	$K_1 = \frac{[H^+][HSO_4^-]}{[H_2SO_4]}$ $K_2 = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$	$1{,}0 \cdot 10^{3}$ $1{,}2 \cdot 10^{-2}$	-3,00 1,94

1	2	3	4
HNO_2	$K=\frac{[H^+][NO_2^-]}{[HNO_2]}$	$6{,}9\cdot10^{-4}$	3,16
H_3PO_4	$K_1=\frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$ $K_2=\frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$ $K_3=\frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$	$7{,}1\cdot10^{-3}$ $6{,}2\cdot10^{-8}$ $5{,}0\cdot10^{-13}$	2,15 7,21 12,00
$H_4P_2O_7$	$K_1=\frac{[H^+][H_3P_2O_7^-]}{[H_4P_2O_7]}$ $K_2=\frac{[H^+][H_2P_2O_7^{2-}]}{[H_3P_2O_7^-]}$ $K_3=\frac{[H^+][HP_2O_7^{3-}]}{[H_2P_2O_7^{2-}]}$ $K_4=\frac{[H^+][P_2O_7^{4-}]}{[HP_2O_7^{3-}]}$	$1{,}2\cdot10^{-1}$ $7{,}9\cdot10^{-3}$ $2{,}0\cdot10^{-7}$ $4{,}8\cdot10^{-10}$	0,91 2,10 6,70 9,32
H_3AsO_4	$K_1=\frac{[H^+][H_2AsO_4^-]}{[H_3AsO_4]}$ $K_2=\frac{[H^+][HAsO_4^{2-}]}{[H_2AsO_4^-]}$ $K_3=\frac{[H^+][AsO_4^{3-}]}{[HAsO_4^{2-}]}$	$5{,}6\cdot10^{-3}$ $1{,}7\cdot10^{-7}$ $3{,}0\cdot10^{-12}$	2,25 6,77 11,53
$HAsO_2$	$K=\frac{[H^+][AsO_2^-]}{[HAsO_2]}$	$6\cdot10^{-10}$	9,22
HCOOH	$K=\frac{[H^+][HCOO^-]}{[HCOOH]}$	$1{,}6\cdot10^{-12}$	11,80
CH_3COOH	$K=\frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$	$1{,}75\cdot10^{-5}$	4,75
HCN	$K=\frac{[H^+][CN^-]}{[HCN]}$	$5{,}0\cdot10^{-10}$	9,30
H_2CO_3 (“apparent” constant)	$K_1=\frac{[H^+][HCO_3^-]}{[H_2CO_3]}$ $K_2=\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$	$4{,}45\cdot10^{-7}$ $4{,}69\cdot10^{-11}$	6,35 10,33

1	2	3	4
$H_2C_2O_4$	$K_1 = \frac{[H^+][HC_2O_4^-]}{[H_2C_2O_4]}$ $K_2 = \frac{[H^+][C_2O_4^{2-}]}{[HC_2O_4^-]}$	$5,6\cdot10^{-2}$ $5,4\cdot10^{-5}$	1,25 4,27
H_2SiO_3	$K_1 = \frac{[H^+][HSiO_3^-]}{[H_2SiO_3]}$ $K_2 = \frac{[H^+][SiO_3^{2-}]}{[HSiO_3^-]}$	$2,2\cdot10^{-10}$ $1,6\cdot10^{-12}$	9,66 11,80
H_2SnO_2	$K_1 = \frac{[H^+][HSnO_2^-]}{[H_2SnO_2]}$	10^{-15}	15,00
H_2SnO_3	$K_1 = \frac{[H^+][HSnO_3^-]}{[H_2SnO_3]}$	10^{-10}	10,00
H_2PbO_2	$K_1 = \frac{[H^+][HPbO_2^-]}{[H_2PbO_2]}$	10^{-11}	11,00
H_3BO_3	$K_1 = \frac{[H^+][H_2BO_3^-]}{[H_3BO_3]}$ $K_2 = \frac{[H^+][HBO_3^{2-}]}{[H_2BO_3^-]}$ $K_3 = \frac{[H^+][BO_3^{3-}]}{[HBO_3^{2-}]}$	$5,8\cdot10^{-10}$ $1,8\cdot10^{-13}$ $1,6\cdot10^{-14}$	9,22 12,74 13,80
$H_2B_4O_7$	$K_1 = \frac{[H^+][HB_4O_7^-]}{[H_2B_4O_7]}$ $K_2 = \frac{[H^+][B_4O_7^{2-}]}{[HB_4O_7^-]}$	$1,0\cdot10^{-4}$ $1,0\cdot10^{-9}$	4,00 9,00
$HAlO_2$	$K = \frac{[H^+][AlO_2^-]}{[HAlO_2]}$	$6,0\cdot10^{-15}$	14,22
H_2MnO_4	$K_1 = \frac{[H^+][HMnO_4^-]}{[H_2MnO_4]}$ $K_2 = \frac{[H^+][MnO_4^{2-}]}{[HMnO_4^-]}$	$\sim10^{-1}$ $7,1\cdot10^{-11}$	1 10,15

1	2	3	4
$HMnO_4$	$K = \frac{[H^+][MnO_4^-]}{[HMnO_4]}$	$2{,}0 \cdot 10^2$	- 2,3
H_2CrO_4	$K_1 = \frac{[H^+][HCrO_4^-]}{[H_2CrO_4]}$ $K_2 = \frac{[H^+][CrO_4^{2-}]}{[HCrO_4^-]}$	$1{,}6 \cdot 10^{-1}$ $3{,}2 \cdot 10^{-7}$	0,80 6,50
H_2MoO_4	$K_1 = \frac{[H^+][HMoO_4^-]}{[H_2MoO_4]}$ $K_2 = \frac{[H^+][MoO_4^{2-}]}{[HMoO_4^-]}$	$2{,}9 \cdot 10^{-3}$ $1{,}4 \cdot 10^{-4}$	2,54 3,86
H_2PbO_2	$K_1 = \frac{[H^+][HPbO_2^-]}{[H_2PbO_2]}$	$1 \cdot 10^{-12}$	12,00
AgOH	$K = \frac{[Ag^+][OH^-]}{[AgOH]}$	$1{,}1 \cdot 10^{-4}$	3,96
$Al(OH)_3$	$K_3 = \frac{[Al^{3+}][OH^-]}{[AlOH^{2+}]}$	$1{,}38 \cdot 10^{-9}$	8,86
$Ba(OH)_2$	$K_2 = \frac{[Ba^{2+}][OH^-]}{[Ba(OH)^-]}$	$2{,}3 \cdot 10^{-1}$	0,64
$Ca(OH)_2$	$K_2 = \frac{[Ca^{2+}][OH^-]}{[Ca(OH)^-]}$	$4{,}0 \cdot 10^{-3}$	1,40
$Cd(OH)_2$	$K_2 = \frac{[Cd^{2+}][OH^-]}{[CdOH^+]}$	$5{,}0 \cdot 10^{-3}$	2,80
$Co(OH)_2$	$K_2 = \frac{[Co^{2+}][OH^-]}{[CoOH^+]}$	$4{,}0 \cdot 10^{-5}$	4,4
$Cr(OH)_3$	$K_3 = \frac{[Cr^{3+}][OH^-]}{[CrOH^{2+}]}$	$1{,}02 \cdot 10^{-10}$	9,99
$Cu(OH)_2$	$K_2 = \frac{[Cu^{2+}][OH^-]}{[CuOH^+]}$	$3{,}4 \cdot 10^{-7}$	6,47

1	2	3	4
$Fe(OH)_2$	$K_2 = \frac{[Fe^{2+}][OH^-]}{[FeOH^+]}$	$1{,}3\cdot10^{-4}$	3,89
$Fe(OH)_3$	$K_2 = \frac{[FeOH^{2+}][OH^-]}{[Fe(OH)_2^+]}$ $K_3 = \frac{[Fe^{3+}][OH^-]}{[FeOH^{2+}]}$	$1{,}8\cdot10^{-11}$ $1{,}4\cdot10^{-12}$	10,74 11,87
$Hg(OH)_2$	$K_1 = \frac{[Hg(OH)^+][OH^-]}{[Hg(OH)_2]}$ $K_2 = \frac{[Hg^{2+}][OH^-]}{[HgOH^+]}$	$7\cdot10^{-12}$ $2\cdot10^{-23}$	11,15 22,70
LiOH	$K = \frac{[Li^+][OH^-]}{[LiOH]}$	$6{,}8\cdot10^{-1}$	0,17
$Mn(OH)_2$	$K_2 = \frac{[Mn^{2+}][OH^-]}{[MnOH^+]}$	$5{,}0\cdot10^{-4}$	3,30
$Mg(OH)_2$	$K_2 = \frac{[Mg^{2+}][OH^-]}{[MgOH^+]}$	$2{,}5\cdot10^{-3}$	2,60
NaOH	$K = \frac{[Na^+][OH^-]}{[NaOH]}$	5,9	- 0,77
$Ni(OH)_2$	$K_2 = \frac{[Ni^{2+}][OH^-]}{[NiOH^+]}$	$2{,}5\cdot10^{-5}$	4,60
NH_4OH (“apparent” constant)	$K = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$	$1{,}76\cdot10^{-5}$	4,755
$Pb(OH)_2$	$K_1 = \frac{[Pb(OH)^+][OH^-]}{[Pb(OH)_2]}$ $K_2 = \frac{[Pb^{2+}][OH^-]}{[Pb(OH)^+]}$	$9{,}6\cdot10^{-4}$ $3\cdot10^{-8}$	3,02 7,52
$Sr(OH)_2$	$K_2 = \frac{[Sr^{2+}][OH^-]}{[SrOH^+]}$	$1{,}5\cdot10^{-1}$	0,82
$Zn(OH)_2$	$K_2 = \frac{[Zn^{2+}][OH^-]}{[Zn(OH)^+]}$	$4{,}0\cdot10^{-5}$	4,40

APPENDIX 9

Solubility product constants (25°C)

Compound	Formula	K_{SP}
1	2	3
Aluminium hydroxide	$Al(OH)_3$	$3\cdot10^{-34}$
Aluminium phosphate	$AlPO_4$	$9{,}84\cdot10^{-21}$
Barium bromate	$Ba(BrO_3)_2$	$2{,}43\cdot10^{-4}$
Barium carbonate	$BaCO_3$	$2{,}58\cdot10^{-9}$
Barium chromate	$BaCrO_4$	$1{,}17\cdot10^{-10}$
Barium fluoride	BaF_2	$1{,}84\cdot10^{-7}$
Barium hydroxide octahydrate	$Ba(OH)_2\cdot8H_2O$	$2{,}55\cdot10^{-4}$
Barium iodate	$Ba(IO_3)_2$	$4{,}01\cdot10^{-9}$
Barium iodate monohydrate	$Ba(IO_3)_2\cdot H_2O$	$1{,}67\cdot10^{-9}$
Barium molybdate	$BaMoO_4$	$3{,}54\cdot10^{-8}$
Barium nitrate	$Ba(NO_3)_2$	$4{,}64\cdot10^{-3}$
Barium selenate	$BaSeO_4$	$3{,}40\cdot10^{-8}$
Barium sulfate	$BaSO_4$	$1{,}08\cdot10^{-10}$
Barium sulfite	$BaSO_3$	$5{,}0\cdot10^{-10}$
Beryllium hydroxide	$Be(OH)_2$	$6{,}92\cdot10^{-22}$
Bismuth arsenate	$BiAsO_4$	$4{,}43\cdot10^{-10}$
Bismuth iodide	BiI	$7{,}71\cdot10^{-19}$
Cadmium arsenate	$Cd_3(AsO_4)_2$	$2{,}2\cdot10^{-33}$
Cadmium carbonate	$CdCO_3$	$1{,}0\cdot10^{-12}$
Cadmium fluoride	CdF_2	$6{,}44\cdot10^{-3}$
Cadmium hydroxide	$Cd(OH)_2$	$7{,}2\cdot10^{-15}$
Cadmium iodate	$Cd(IO_3)_2$	$2{,}5\cdot10^{-8}$
Cadmium oxalate trihydrate	$CdC_2O_4\cdot3H_2O$	$1{,}42\cdot10^{-8}$
Cadmium phosphate	$Cd_3(PO_4)_2$	$2{,}53\cdot10^{-33}$
Cadmium sulfide	CdS	$1\cdot10^{-27}$
Caesium perchlorate	$CsClO_4$	$3{,}95\cdot10^{-3}$
Caesium periodate	$CsIO_4$	$5{,}16\cdot10^{-6}$
Calcium carbonate (calcite)	$CaCO_3$	$3{,}36\cdot10^{-9}$
Calcium carbonate (aragonite)	$CaCO_3$	$6{,}0\cdot10^{-9}$
Calcium fluoride	CaF_2	$3{,}45\cdot10^{-11}$
Calcium hydroxide	$Ca(OH)_2$	$5{,}02\cdot10^{-6}$
Calcium iodate	$Ca(IO_3)_2$	$6{,}47\cdot10^{-6}$

1	2	3
Calcium iodate hexahydrate	$Ca(IO_3)_2\cdot 6H_2O$	$7,10\cdot 10^{-7}$
Calcium molybdate	$CaMoO_4$	$1,46\cdot 10^{-8}$
Calcium oxalate monohydrate	$CaC_2O_4\cdot H_2O$	$2,32\cdot 10^{-9}$
Calcium phosphate	$Ca_3(PO_4)_2$	$2,07\cdot 10^{-33}$
Calcium sulfate	$CaSO_4$	$4,93\cdot 10^{-5}$
Calcium sulfate dihydrate	$CaSO_4\cdot 2H_2O$	$3,14\cdot 10^{-5}$
Calcium sulfate hemihydrate	$CaSO_4\cdot 0,5H_2O$	$3,1\cdot 10^{-7}$
Cobalt(II) arsenate	$Co_3(AsO_4)_2$	$6,80\cdot 10^{-29}$
Cobalt(II) carbonate	$CoCO_3$	$1,0\cdot 10^{-10}$
Cobalt(II) hydroxide (blue)	$Co(OH)_2$	$5,92\cdot 10^{-15}$
Cobalt(II) iodate dihydrate	$Co(IO_3)_2\cdot 2H_2O$	$1,21\cdot 10^{-2}$
Cobalt(II) phosphate	$Co_3(PO_4)_2$	$2,05\cdot 10^{-35}$
Cobalt(II) sulfide (α)	CoS	$5\cdot 10^{-22}$
Cobalt(II) sulfide (β)	CoS	$3\cdot 10^{-26}$
Copper(I) bromide	$CuBr$	$6,27\cdot 10^{-9}$
Copper(I) chloride	$CuCl$	$1,72\cdot 10^{-7}$
Copper(I) cyanide	$CuCN$	$3,47\cdot 10^{-20}$
Copper(I) hydroxide *	Cu_2O	$2\cdot 10^{-15}$
Copper(I) iodide	CuI	$1,27\cdot 10^{-12}$
Copper(I) thiocyanate	$CuSCN$	$1,77\cdot 10^{-13}$
Copper(II) arsenate	$Cu_3(AsO_4)_2$	$7,95\cdot 10^{-36}$
Copper(II) hydroxide	$Cu(OH)_2$	$4,8\cdot 10^{-20}$
Copper(II) iodate monohydrate	$Cu(IO_3)_2\cdot H_2O$	$6,94\cdot 10^{-8}$
Copper(II) oxalate	CuC_2O_4	$4,43\cdot 10^{-10}$
Copper(II) phosphate	$Cu_3(PO_4)_2$	$1,40\cdot 10^{-37}$
Copper(II) sulfide	CuS	$8\cdot 10^{-37}$
Europium(III) hydroxide	$Eu(OH)_3$	$9,38\cdot 10^{-27}$
Gallium(III) hydroxide	$Ga(OH)_3$	$7,28\cdot 10^{-36}$
Iron(II) carbonate	$FeCO_3$	$3,13\cdot 10^{-11}$
Iron(II) fluoride	FeF_2	$2,36\cdot 10^{-6}$
Iron(II) hydroxide	$Fe(OH)_2$	$4,87,10^{-17}$
Iron(II) sulfide	FeS	$8\cdot 10^{-19}$
Iron(III) hydroxide	$Fe(OH)_3$	$2,79\cdot 10^{-39}$
Iron(III) phosphate dihydrate	$FePO_4\cdot 2H_2O$	$9,91\cdot 10^{-16}$
Lanthanum iodate	$La(IO_3)_3$	$7,50\cdot 10^{-12}$
Lead(II) bromide	$PbBr_2$	$6,60\cdot 10^{-6}$
Lead(II) carbonate	$PbCO_3$	$7,40\cdot 10^{-14}$

1	2	3
Lead(II) chloride	$PbCl_2$	$1{,}70 \cdot 10^{-5}$
Lead(II) chromate	$PbCrO_4$	$3 \cdot 10^{-13}$
Lead(II) fluoride	PbF_2	$3{,}3 \cdot 10^{-8}$
Lead(II) hydroxide	$Pb(OH)_2$	$1{,}43 \cdot 10^{-20}$
Lead(II) iodate	$Pb(IO_3)_2$	$3{,}69 \cdot 10^{-13}$
Lead(II) iodide	PbI_2	$9{,}8 \cdot 10^{-9}$
Lead(II) oxalate	PbC_2O_4	$8{,}5 \cdot 10^{-9}$
Lead(II) selenate	$PbSeO_4$	$1{,}37 \cdot 10^{-7}$
Lead(II) sulfate	$PbSO_4$	$2{,}53 \cdot 10^{-8}$
Lead(II) sulfide	PbS	$3 \cdot 10^{-28}$
Lithium carbonate	Li_2CO_3	$8{,}15 \cdot 10^{-4}$
Lithium fluoride	LiF	$1{,}84 \cdot 10^{-3}$
Lithium phosphate	Li_3PO_4	$2{,}37 \cdot 10^{-4}$
Magnesium ammonium phosphate	$MgNH_4PO_4$	$3 \cdot 10^{-13}$
Magnesium carbonate	$MgCO_3$	$6{,}82 \cdot 10^{-6}$
Magnesium carbonate trihydrate	$MgCO_3 \cdot 3H_2O$	$2{,}38 \cdot 10^{-6}$
Magnesium carbonate pentahydrate	$MgCO_3 \cdot 5H_2O$	$3{,}79 \cdot 10^{-6}$
Magnesium fluoride	MgF_2	$5{,}16 \cdot 10^{-11}$
Magnesium hydroxide	$Mg(OH)_2$	$5{,}61 \cdot 10^{-12}$
Magnesium oxalate dihydrate	$MgC_2O_4 \cdot 2H_2O$	$4{,}83 \cdot 10^{-6}$
Magnesium phosphate	$Mg_3(PO_4)_2$	$1{,}04 \cdot 10^{-24}$
Manganese(II) carbonate	$MnCO_3$	$2{,}24 \cdot 10^{-11}$
Manganese(II) iodate	$Mn(IO_3)_2$	$4{,}37 \cdot 10^{-7}$
Manganese(II) hydroxide	$Mn(OH)_2$	$2 \cdot 10^{-13}$
Manganese(II) oxalate dihydrate	$MnC_2O_4 \cdot 2H_2O$	$1{,}70 \cdot 10^{-7}$
Manganese(II) sulfide (pink)	MnS	$3 \cdot 10^{-11}$
Manganese(II) sulfide (green)	MnS	$3 \cdot 10^{-14}$
Mercury(I) bromide	Hg_2Br_2	$6{,}40 \cdot 10^{-23}$
Mercury(I) carbonate	Hg_2CO_3	$3{,}6 \cdot 10^{-17}$
Mercury(I) chloride	Hg_2Cl_2	$1{,}43 \cdot 10^{-18}$
Mercury(I) fluoride	Hg_2F_2	$3{,}10 \cdot 10^{-6}$
Mercury(I) iodide	Hg_2I_2	$5{,}2 \cdot 10^{-29}$
Mercury(I) oxalate	$Hg_2C_2O_4$	$1{,}75 \cdot 10^{-13}$

1	2	3
Mercury(I) sulfate	Hg_2SO_4	$6,5\cdot10^{-7}$
Mercury(I) thiocyanate	$Hg_2(SCN)_2$	$3,2\cdot10^{-20}$
Mercury(II) bromide	$HgBr_2$	$6,2\cdot10^{-20}$
Mercury(II) hydroxide **	HgO	$3,6\cdot10^{-26}$
Mercury(II) iodide	HgI_2	$2,9\cdot10^{-29}$
Mercury(II) sulfide (black)	HgS	$2\cdot10^{-53}$
Mercury(II) sulfide (red)	HgS	$2\cdot10^{-54}$
Neodymium carbonate	$Nd_2(CO_3)_3$	$1,08\cdot10^{-33}$
Nickel(II) carbonate	$NiCO_3$	$1,42\cdot10^{-7}$
Nickel(II) hydroxide	$Ni(OH)_2$	$5,48\cdot10^{-16}$
Nickel(II) iodate	$Ni(IO_3)_2$	$4,71\cdot10^{-5}$
Nickel(II) phosphate	$Ni_3(PO_4)_2$	$4,74\cdot10^{-32}$
Nickel(II) sulfide (α)	NiS	$4\cdot10^{-20}$
Nickel(II) sulfide (β)	NiS	$1,3\cdot10^{-25}$
Palladium(II) thiocyanate	$Pd(SCN)_2$	$4,39\cdot10^{-23}$
Potassium hexachloroplatinate	K_2PtCl_6	$7,48\cdot10^{-6}$
Potassium perchlorate	$KClO_4$	$1,05\cdot10^{-2}$
Potassium periodate	KIO_4	$3,71\cdot10^{-4}$
Praseodymium hydroxide	$Pr(OH)_3$	$3,39\cdot10^{-24}$
Radium iodate	$Ra(IO_3)_2$	$1,16\cdot10^{-9}$
Radium sulfate	$RaSO_4$	$3,66\cdot10^{-11}$
Rubidium perchlorate	$RuClO_4$	$3,00\cdot10^{-3}$
Scandium fluoride	ScF_3	$5,81\cdot10^{-24}$
Scandium hydroxide	$Sc(OH)_3$	$2,22\cdot10^{-31}$
Silver(I) acetate	$AgCH_3COO$	$1,94\cdot10^{-3}$
Silver(I) arsenate	Ag_3AsO_4	$1,03\cdot10^{-22}$
Silver(I) bromate	$AgBrO_3$	$5,38\cdot10^{-5}$
Silver(I) bromide	AgBr	$5,35\cdot10^{-13}$
Silver(I) carbonate	Ag_2CO_3	$8,46\cdot10^{-12}$
Silver(I) chloride	AgCl	$1,77\cdot10^{-10}$
Silver(I) chromate	Ag_2CrO_4	$1,12\cdot10^{-12}$
Silver(I) cyanide	AgCN	$5,97\cdot10^{-17}$
Silver(I) iodate	$AgIO_3$	$3,17\cdot10^{-8}$
Silver(I) iodide	AgI	$8,52\cdot10^{-17}$
Silver(I) oxalate	$Ag_2C_2O_4$	$5,40\cdot10^{-12}$
Silver(I) phosphate	Ag_3PO_4	$8,89\cdot10^{-17}$
Silver(I) sulfate	Ag_2SO_4	$1,20\cdot10^{-5}$
Silver(I) sulfite	Ag_2SO_3	$1,50\cdot10^{-14}$

1	2	3
Silver(I) sulfide	Ag_2S	$8\cdot10^{-51}$
Silver(I) thiocyanate	AgSCN	$1{,}03\cdot10^{-12}$
Strontium arsenate	$Sr_3(AsO_4)_2$	$4{,}29\cdot10^{-19}$
Strontium carbonate	$SrCO_3$	$5{,}60\cdot10^{-10}$
Strontium fluoride	SrF_2	$4{,}33\cdot10^{-9}$
Strontium iodate	$Sr(IO_3)_2$	$1{,}14\cdot10^{-7}$
Strontium iodate monohydrate	$Sr(IO_3)_2\cdot H_2O$	$3{,}77\cdot10^{-7}$
Strontium iodate hexahydrate	$Sr(IO_3)_2\cdot 6H_2O$	$4{,}55\cdot10^{-7}$
Strontium oxalate	SrC_2O_4	$5\cdot10^{-8}$
Strontium sulfate	$SrSO_4$	$3{,}44\cdot10^{-7}$
Thallium(I) bromate	$TlBrO_3$	$1{,}10\cdot10^{-4}$
Thallium(I) bromide	TlBr	$3{,}71\cdot10^{-6}$
Thallium(I) chloride	TlCl	$1{,}86\cdot10^{-4}$
Thallium(I) chromate	Tl_2CrO_4	$8{,}67\cdot10^{-13}$
Thallium(I) hydroxide	$Tl(OH)_3$	$1{,}68\cdot10^{-44}$
Thallium(I) iodate	$TlIO_3$	$3{,}12\cdot10^{-6}$
Thallium(I) iodide	TlI	$5{,}54\cdot10^{-8}$
Thallium(I) thiocyanate	TlSCN	$1{,}57\cdot10^{-4}$
Thallium(I) sulfide	Tl_2S	$6\cdot10^{-22}$
Tin(II) hydroxide	$Sn(OH)_2$	$5{,}45\cdot10^{-27}$
Yttrium carbonate	$Y_2(CO_3)_3$	$1{,}03\cdot10^{-31}$
Yttrium fluoride	YF_3	$8{,}62\cdot10^{-21}$
Yttrium iodate	$Y(IO_3)_3$	$1{,}12\cdot10^{-10}$
Zinc arsenate	$Zn_3(AsO_4)_2$	$2{,}8\cdot10^{-28}$
Zinc carbonate	$ZnCO_3$	$1{,}46\cdot10^{-10}$
Zinc carbonate monohydrate	$ZnCO_3\cdot H_2O$	$5{,}42\cdot10^{-11}$
Zinc hydroxide	$Zn(OH)_2$	$3\cdot10^{-17}$
Zinc iodate dihydrate	$Zn(IO_3)_2\cdot 2H_2O$	$4{,}1\cdot10^{-6}$
Zinc oxalate dihydrate	$ZnC_2O_4\cdot 2H_2O$	$1{,}38\cdot10^{-9}$
Zinc selenide	ZnSe	$3{,}6\cdot10^{-26}$
Zinc selenite monohydrate	$ZnSe\cdot H_2O$	$1{,}59\cdot10^{-7}$
Zinc sulfide (α)	ZnS	$2\cdot10^{-25}$
Zinc sulfide (β)	ZnS	$3\cdot10^{-23}$

(*) $Cu_2O + H_2O \rightleftarrows 2\ Cu^+ + 2\ OH^-$

(**) $HgO + H_2O \rightleftarrows Hg^{2+} + 2\ OH^-$

APPENDIX 10

Theoretical foundations of Redoxmetry

Application of REDOX titrations

It's time to look at some specific examples so you appreciate the scope of the approach.

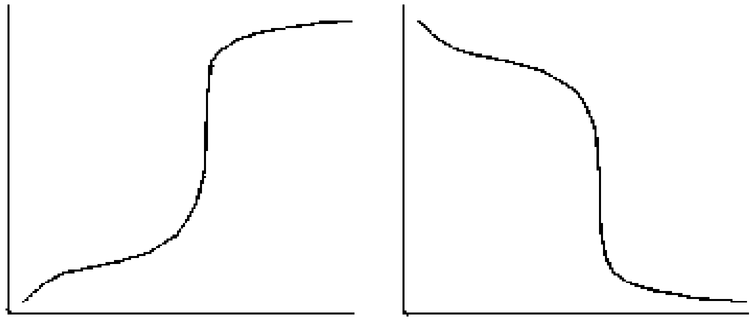
The first step is to dissolve your sample which can result in mixed oxidation states.

Example - an iron sample will result in both Fe^{2+} and Fe^{3+} being formed.

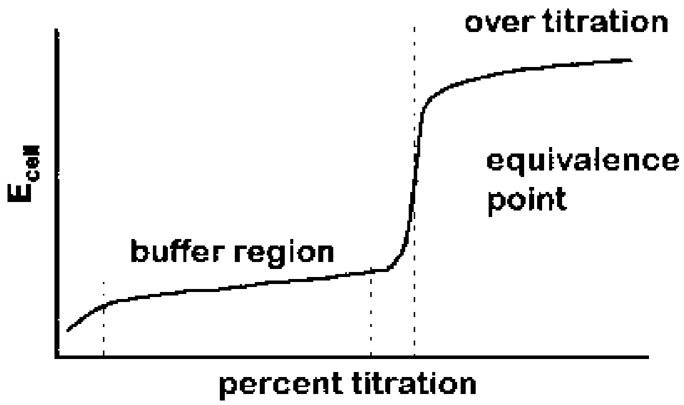
For a titration to yield meaningful results, we need to have our analyte all in a single oxidation state.

Titration curves

As with acid/base titrations, we can get either to the following types of curves.



Based on the type of reaction.



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For each titration curve, there are four significant regions.

The start - 0% titration

Buffer region - >0%, < equivalence point

The equivalence point

Overtitration

Lets look at each, using our simple example - the titration of Fe^{2+} with Ce^{4+}.

0% titration

Unlike acid/base titrations, we really can't do much with this region.

While some Fe^{3+} must be present, we can only guess what the concentration is.

No Ce^{4+} or Ce^{3+} are present, so we don't have a complete reaction.

Buffer region

Between 0% and 100% titration, we can use the Nernst equation for Fe^{2+}/Fe^{3+}.

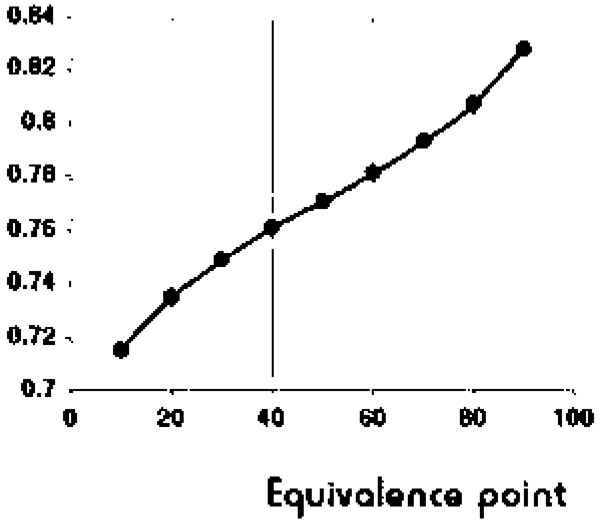
$$E_{Fe} = 0.771 - 0.0592 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

There is no significant level of Ce^{4+} to work with anyway.

We can simplify our calculations by using the % titration.

$$E_{Fe} = 0.771 - 0.0592 \log \frac{\%Fe^{2+}}{\%Fe^{3+}}$$

Fe^{3+}	Fe^{2+}	Fe^{2+}/Fe^{3+}	E
10	90	9	0.715
20	80	4	0.735
30	70	2.33	0.749
40	60	1.5	0.761
50	50	1	0.771
60	40	0.67	0.781
70	30	0.43	0.793
80	20	0.25	0.807
90	10	0.11	0.828



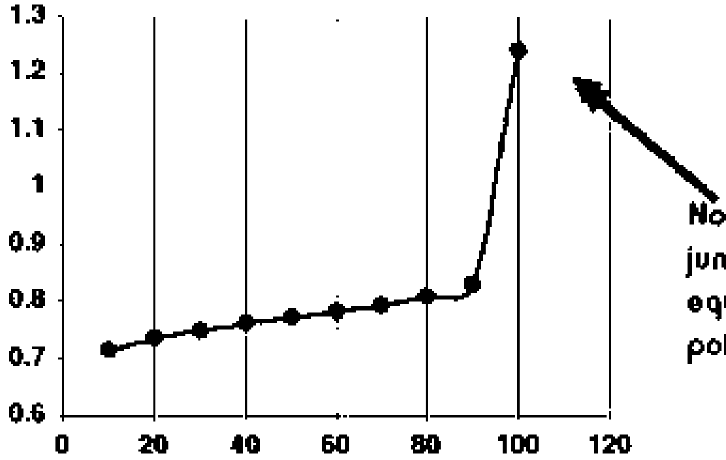
There was only a change of 0.113 V from 10 to 90% titration

Here we use the entire equilibrium expression.

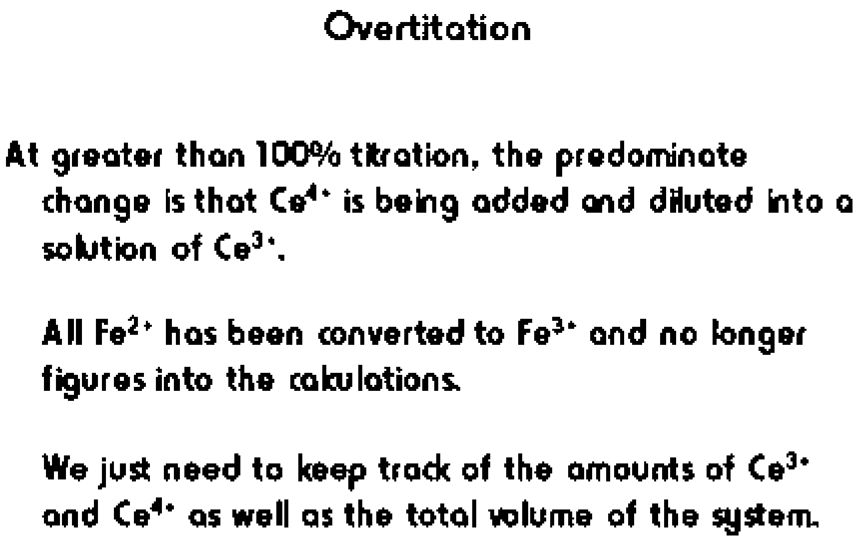
Earlier we found that for this equilibrium,

$$E_{eq} = \frac{1.70V + 0.771V}{2}$$

$$= 1.24\ V$$



Note the large jump in E at the equivalence point.

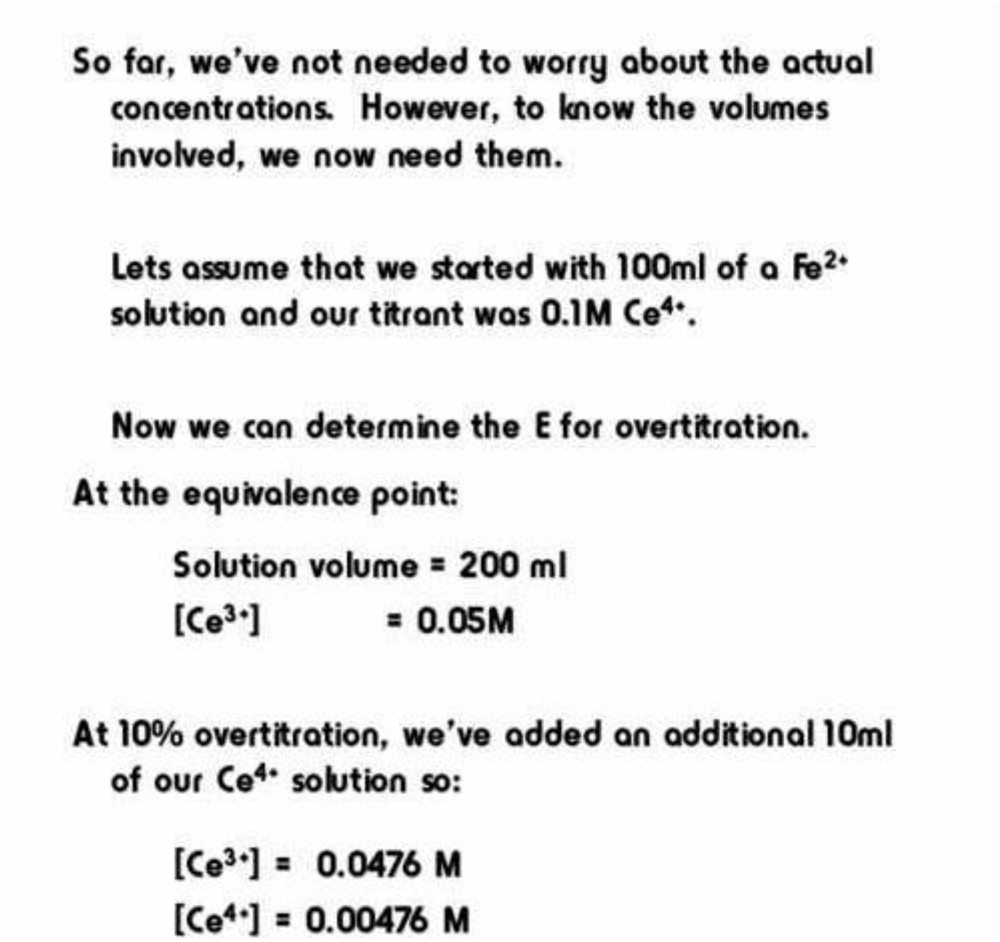


Overtitation

At greater than 100% titration, the predominate change is that Ce^{4+} is being added and diluted into a solution of Ce^{3+}.

All Fe^{2+} has been converted to Fe^{3+} and no longer figures into the calulations.

We just need to keep track of the amounts of Ce^{3+} and Ce^{4+} as well as the total volume of the system.



So far, we've not needed to worry about the actual concentrations. However, to know the volumes involved, we now need them.

Lets assume that we started with 100ml of a Fe^{2+} solution and our titrant was 0.1M Ce^{4+}.

Now we can determine the E for overtitration.

At the equivalence point:

Solution volume = 200 ml
$[Ce^{3+}]$ = 0.05M

At 10% overtitration, we've added an additional 10ml of our Ce^{4+} solution so:

$[Ce^{3+}]$ = 0.0476 M
$[Ce^{4+}]$ = 0.00476 M

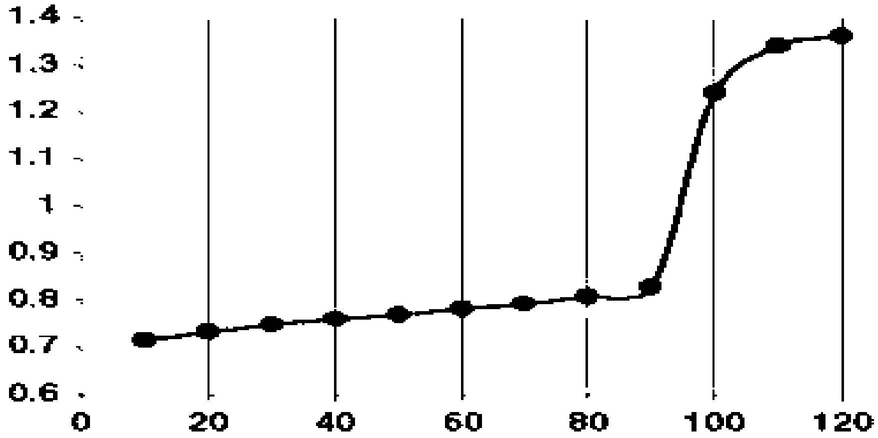
We can again use the Nernst equation to determine the E for our system.

In this case, however, we'll use the values for Ce^{3+} and Ce^{4+}.

$$E = 1.40 - 0.0592 \log \frac{0.0476}{0.00476}$$
$$= 1.34$$

At 20% overtitration. E would be 1.36.

Complete titration curve



Redox indicators

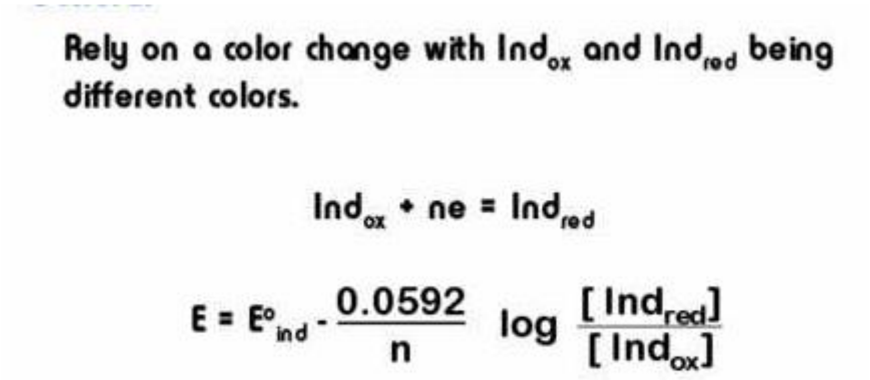
Two types of indicators

General

Varies as a function of E_{cell}

Specific

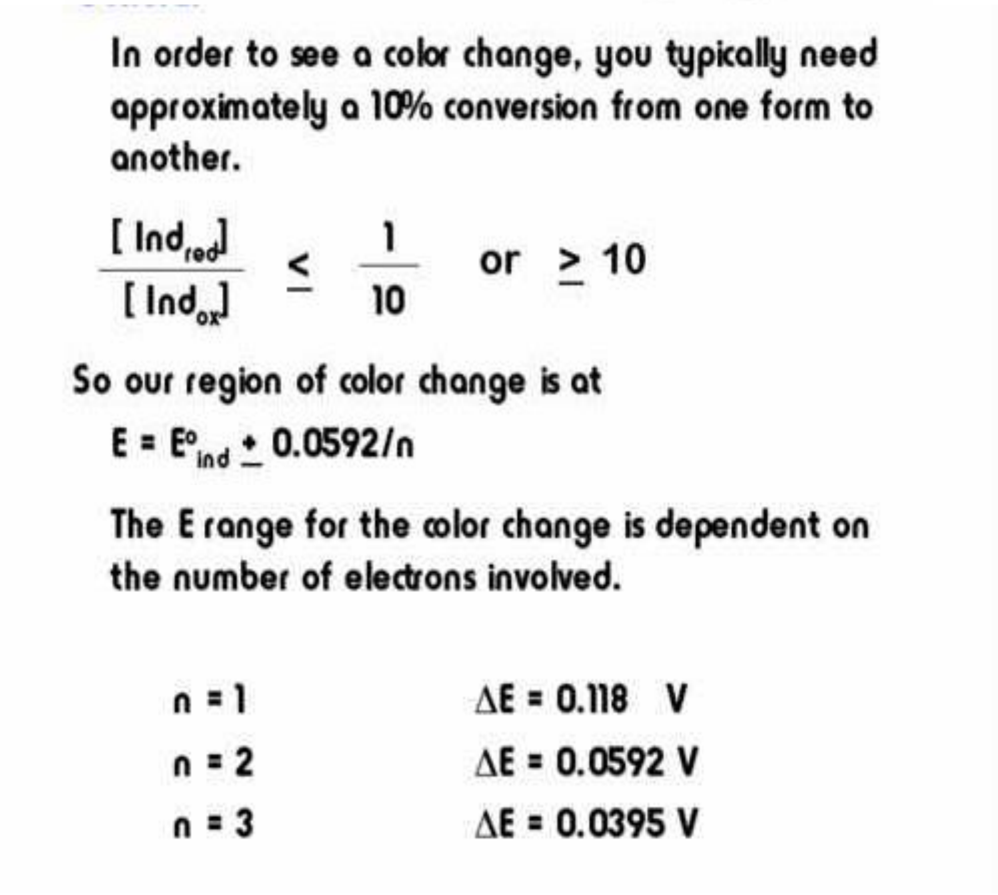
React with a specific chemical species involved in the titration



Rely on a color change with Ind_{ox} and Ind_{red} being different colors.

$$Ind_{ox} + ne = Ind_{red}$$

$$E = E^{o}_{ind} - \frac{0.0592}{n} \log \frac{[Ind_{red}]}{[Ind_{ox}]}$$



In order to see a color change, you typically need approximately a 10% conversion from one form to another.

$$\frac{[Ind_{red}]}{[Ind_{ox}]} \leq \frac{1}{10} \quad \text{or} \quad \geq 10$$

So our region of color change is at

$E = E^{o}_{ind} \pm 0.0592/n$

The E range for the color change is dependent on the number of electrons involved.

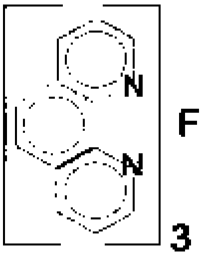
$n = 1$ $\Delta E = 0.118$ V

$n = 2$ $\Delta E = 0.0592$ V

$n = 3$ $\Delta E = 0.0395$ V

Examples

1,10 phenanthrolene - Fe salt



$(Phen)_3Fe^{3+} + e \rightleftharpoons (Phen)_3Fe^{2+}$

pale blue red

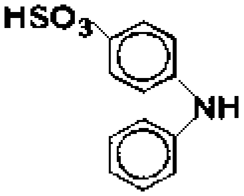
$E^o = 1.06V$

Examples

Diphenylamine sulphonic acid

This derivative of diphenylamine is used since it is more water soluble.

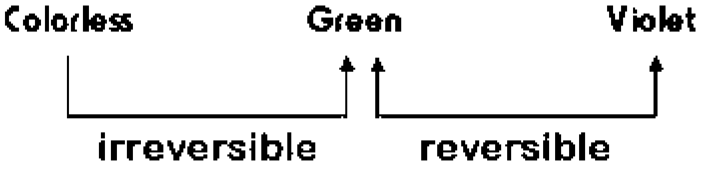
Used with the iron by dichromate method



$E^o = 0.80V$

Examples

Diphenylamine sulphonic acid undergoes two sequential color changes.



Specific indicator example

Starch

Starch + $I_3^- \rightleftharpoons$ blue complex

It is an easy to detect and rapid indicator. This explains why iodine is a common titrant even though it is a weak oxidant.

Specific indicator example

Indirect use of starch

Another common use is to prepare the starch-iodine complex as an indicator. This is done when the titrant is an oxidant.

thiocyanate + $Fe^{2+} \xrightarrow{\text{Starch-I}}$

Jones Reductor

$Zn(Hg) \longrightarrow Zn^{2+} + Hg + 2e$

An amalgam is used to prevent

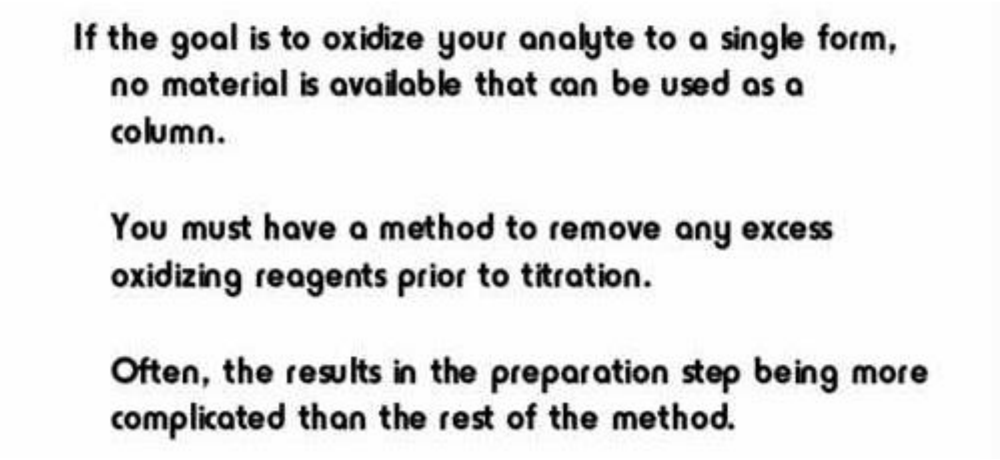
$Zn + 2H^+ \longrightarrow Zn^{2+} + H_{2(g)}$

Walden Reductor

$Ag \xrightarrow{HCl} AgCl(s) + e$

Cl^- is needed to prevent Ag^+ from entering the solution - typically use HCl

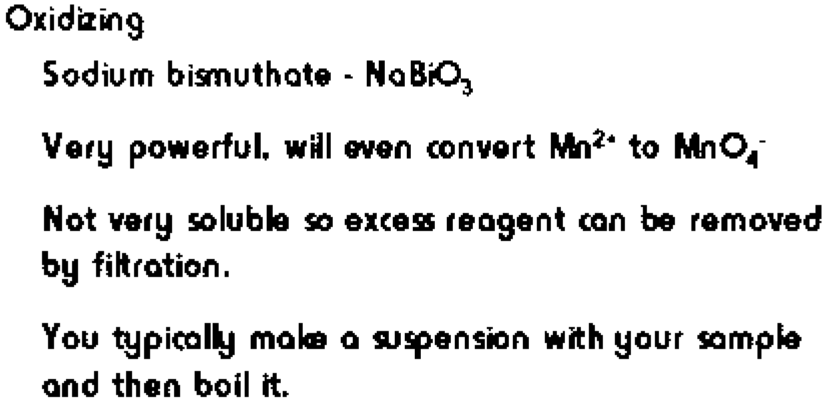
Jones Reductor is stronger that Walden.



If the goal is to oxidize your analyte to a single form, no material is available that can be used as a column.

You must have a method to remove any excess oxidizing reagents prior to titration.

Often, the results in the preparation step being more complicated than the rest of the method.



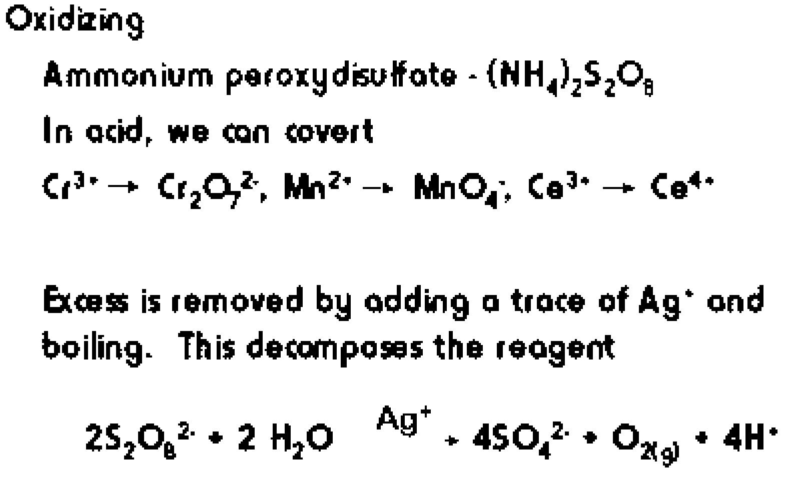
Oxidizing

Sodium bismuthate - $NaBiO_3$

Very powerful, will even convert Mn^{2+} to MnO_4^-

Not very soluble so excess reagent can be removed by filtration.

You typically make a suspension with your sample and then boil it.



Oxidizing

Ammonium peroxydisulfate - $(NH_4)_2S_2O_8$

In acid, we can covert

$Cr^{3+} \rightarrow Cr_2O_7^{2-}$, $Mn^{2+} \rightarrow MnO_4^-$, $Ce^{3+} \rightarrow Ce^{4+}$

Excess is removed by adding a trace of Ag^+ and boiling. This decomposes the reagent

$$2S_2O_8^{2-} + 2\,H_2O \xrightarrow{Ag^+} 4SO_4^{2-} + O_{2(g)} + 4H^+$$

Oxidizing

Peroxide

Not as strong as the other examples

Must be used in acidic solution

$H_2O_2 + 2\ H^+ + 2e = 2\ H_2O$

Excess can be removed by boiling.

Common titrants

Oxidizing titrants

$Cr_2O_7^{2-}$

Primary standard material

Need an indicator such as diphenylamine sulfonic acid.

Very stable solutions. If air is kept out, it can last for years.

$E = 1.44\ V$

Oxidizing titrants

MnO_4^- $E^o = 1.51\ V$

Solutions must be standardized - typically use $Na_2C_2O_4$ (a primary standard material.)

Reagent slowly degrades and MnO_2 must be removed

No indicator is needed - excess reagent produces a pink solution.

Reducing titrants

Fe^{2+}

Used in the form of as

$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 1.0 N H_2SO_4

Solution must be standardized each day.

Reducing titrants

Iodide - indirect method

$2I^- = I_2 + 2e^-$

Can't be used directly due to it's intense color and reaction with air.

Its more common to add excess iodide and use starch as an indicator.

Any iodine that is produced can be determined by titration with $Na_2S_2O_3$.

Iodide - indirect method

What happens is that

$$2I^- + Ox \longrightarrow I_2 + Red$$

$$\downarrow$$

$$I_2 + 2\,S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

It looks like it would just be easier to reduce our analyte with $S_2O_3^{2-}$ directly.

Iodide - indirect method

$S_2O_3^{2-}$ can't be used directly with most material.

It results in a mixture of $S_2O_6^{2-}$ and SO_4^{2-} which can't be predicted

Reaction with I_2 is unique in that only $S_2O_6^{2-}$ is formed.

Reducing titrants

- $S_2O_3^{2-}$ is not a primary standard material.
- It must be standardized using KIO_3.

$$IO_3^- + 5\ I^- + 6\ H^+ = 3\ I_3^- + 2\ H_2O$$

- KI is added to form I_3^-, which is water soluble.
- Although $S_2O_3^{2-}$ solutions are resistant to air oxidation, the tend to decompose:

$$S_2O_3^{2-} + H^+ \rightleftharpoons HSO_3^- + S_{(s)}$$

Another example

Many REDOX reagents have been reported. Some get very specific. One good example is the Karl Fisher method for water.

Karl Fisher reagent

A mixture of iodine, sulfur dioxide, pyridine and methanol.

$$C_5H_5N{\cdot}I_2 + C_5H_5NSO_2 + C_5H_5N{\cdot}HI + H_2O$$

$$2\ C_5H_5N{\cdot}HI + C_5H_5{\cdot}SO_3$$

Methanol is added to remove the reactive $C_5H_5N \cdot SO_3$ complex.

$$C_5H_5N \cdot SO_3 + CH_3OH \longrightarrow C_5H_5N(H)SO_4CH_3$$

This is done because the SO_3 complex can react with water as well as many other species.

The reagent is proprietary so it must be purchased.

Fortunately, it is relatively stable.

It is most commonly used with a special auto titrator system.

Endpoint detection.

Intense color produced by I_2 complex.

APPENDIX 11

Example of exam test

Level, %	**Content of question**
50	**Question 1. Group qualitative reactant of Cu^{2+} cations is (according to ammonium-phosphate classification):**
1	Red blood salt;
2	Yellow blood salt;
3	Ammonium hydrophosphate;
4	Concentrated ammonia.
75	**Question 2. Qualitative reaction of CH_3COO^- anion with strong acid is accompanied by visual effect of:**
1	Blue colorizing of solution;
2	Brown ring;
3	Special odor;
4	Crimson colorizing of solution.
50	**Question 3. For semimicro qualitative analysis it is used:**
1	Near 100 g of solid and 100 mL of liquid reactants;
2	Near 10 g of solid and 1 L of liquid reactants;
3	Near 0,001 g of solid and 0,1 mL of liquid reactants;
4	Near 0,05 g of solid and 1 mL of liquid reactants.
75	**Question 4. Solution of potassium permanganate in the burette is levelled on:**
1	The highest point of the meniscus;
2	The lowest point of the meniscus;
3	The middle point of the meniscus;
4	The zero point of the meniscus.
75	**Question 5. Accuracy of weighting of analytical balances is:**
1	±0,0001 g;
2	±5 g;
3	±0,01 g;
4	±0,1 g.
100	**Question 6. Mass of H_2SO_4 (M=98,00 g/mol), dissolved in 2000 mL of solution, if for titration of 10 mL of this solution it was used 12,3 mL of 0,01 N NaOH):**
1	1,2054 g;
2	2,4108 g;

3	3,4567 g;
4	0,1205 g.
100	**Question 7. What mixture has buffer properties:**
1	NH_4Cl + NH_4HCO_3;
2	NH_4Cl + NH_4OH;
3	HCl + NH_4Cl;
4	NH_4Cl + $NH_4H_2PO_4$.
100	**Question 8. For qualitative determination of Mg^{2+} ion of Ammonia or Sodium Hydrophosphate it is prevented the presence in solution:**
1	Cations of alkali metals;
2	Anions;
3	Cations of the 2d group;
4	All cations of the 2^{d}, 3^{d} and 4th groups (according to ammonia-phosphate classification).
100	**Question 9. In analytical determinations it doesn’t use chemicals of such purity:**
1.	Technical grade;
2.	Extra Pure grade;
3.	Pharmacopoeia grade;
4.	For Analytical Purpose.
75	**Question 10. Mass of $CaCl_2·6H_2O$ (M=219,08 g/mol) for precipitation of Calcium in the form of $CaC_2O_4·H_2O$ (M=146,11 g/mol) is:**
1.	1,4994 g;
2.	0,7497 g;
3.	0,4998 g;
4.	0,9996 g.
100	**Question 11. Buffer solution has such main property:**
1	To stabilize ionic strength or pH of solution;
2	To stabilize density of solution;
3	To stabilize temperature of solution;
4	To stabilize color of solution.
75	**Question 12. It is necessary for preparation of coarse-crystalline precipitate:**
1	To precipitate of hot diluted solutions;
2	To precipitate of cold diluted solutions;
3	To precipitate of hot concentrated solutions;
4	To precipitate of cold concentrated solutions.
100	**Question 13. pH of 0,01 N HIO_3 (pK=10,64) is:**

1	6,32;
2	10,64;
3	7,00;
4	1,12.
75	**Question 14. ppm – this is…:**
1	Percent per mass;
2	Parts per million;
3	Parts per mass;
4	Percent per million.
75	**Question 15. Equivalent mass of H_3BO_3 (M=61,83 g/mol) in neutralization processes is equal to:**
1	61,83 g/g-eq;
2	10,31 g/g-eq;
3	20,61 g/g-eq;
4	122,66 g/g-eq.
75	**Question 16. Such system of cation classification doesn't exist:**
1	Acid-base;
2	Phosphate;
3	Hydrochloride;
4	Buffer.
75	**Question 17. Qualitative reaction of Pb^{2+} anion with KI after re-crystallization in presence of acetic acid is accompanied by visual effect of:**
1	Blue colorizing of solution;
2	Brown ring;
3	Yellow-goldish precipitation ("Gold rain");
4	Crimson colorizing of solution.
100	**Question 18. Equivalent concentration is shown:**
1	Quantity of moles of soluble substance per 1 L of solution;
2	Quantity of equivalents of soluble substance per 1 L of solution;
3	Quantity of moles of soluble substance per 1 kg of solution;
4	Quantity of moles of soluble substance in per 100 mL of solution.
100	**Question 19. According to Tananaev's recommendations, mass of amorphous precipitate is the best of all would be:**
1	Near 0,2 g;
2	Near 0,5 g;
3	Near 1 g;
4	Near 1 mol.
75	**Question 20. Sign of heterogeneous system is:**
1	Presence of precipitate and solution simultaneously;

2	One aggregate state of all phases;
3	Absence of separated surfaces between phases;
4	Mixing of all components.
100	**Question 21. SO_3^{2-} and SO_4^{2-} anions may be separated one from other by adding:**
1	Concentrated ammonia;
2	Silver nitrate;
3	Sulphate acid;
4	Barium chloride and action of diluted HCl into formed precipitates.
75	**Question 22. Equivalent mass of Ca^{2+} cation (A (Ca)=40,08) in reaction with Trilon B is:**
1	40,08 g-eq/g;
2	20,04 g-eq/g;
3	10,02 g-eq/g;
4	5,01 g-eq/g.
75	**Question 23. Metallochromic indicators in complexonometry are:**
1	Weak bases;
2	Weak acids;
3	Red-Ox systems;
4	Ligands, formed colored unstable compexes with metal cations.
75	**Question 24. The most sensitive reactant of Na^+ determination is:**
1	$K[Sb(OH)_6]$;
2	$Zn(UO_2)_3(CH_3COO)_8$ in presence of acetic acid;
3	Chugaev’s reactant;
4	$NH_4H_2PO_4$.
100	**Question 25. Red-Ox potential of the system MnO_4^-/Mn^{2+} at pH=3 ($E^0(MnO_4^-/Mn^{2+})=+1,52V$), when $[MnO_4]=[Mn^{2+}]=1$ mol/L, is:**
1	+1,80 V;
2	-1,80 V;
3	+1,24 V;
4	-1,52 V.
75	**Question 26. The best indicator for titration of 0,1 N acetic acid by 0,1 N Sodium hydroxide is ($pH_{equivalent\ point}=8,16$):**
1	Methyl Violet (pT=1,4);
2	Cresol red (pT=7,5);
3	Methacresol purple (pT=8,2);

4	Orange G (pT=12,8).
100	**Question 27. Equivalent mass of $KMnO_4$ for titration in acidic medium is ($M(KMnO_4)=158$ g/mol):**
1	158 g/g-eq;
2	52,7 g/g-eq;
3	79,0 g/g-eq;
4	31,6 g/g-eq.
75	**Question 28. Percent concentration is shown:**
1	Mass of solute in 100 mL of solution;
2	Mass of solute in 100 g of solution;
3	Mass of solute in 1 kg of solution;
4	Mass of solute in 1000 mL of solution.
100	**Question 29. Equivalent point of titration in neutralization reaction corresponds to:**
1	Starting of indicator color change;
2	Finishing of indicator color change;
3	pH in the starting of titration jump;
4	pH in the centre of titration jump;
75	**Question 30. The most sensible test for borate anion determinations is:**
1	Reaction with Sodium hydroxide;
2	Flame test with concentrated sulphate acid and alcohol;
3	Test with $BaCl_2$;
4	Test with $AgNO_3$.

INDEX

LITERATURE

1. Жаровський Ф.Г. Аналітична хімія / Жаровський Ф.Г., Пилипенко А.Т., П'ятницький І.В. – К.:Вища шк., 1982. – 544с.
2. Цитович И.К. Курс аналитической химии / Цитович И.К. – М.: Высш. шк., 1985. – 400с.
3. Пилипенко А.Т. Аналитическая химия / Пилипенко А.Т., Пятницкий И.В. – М.:Химия, 1991. – 846с.
4. Крешков А.П. Основы аналитической химии В 3-х тт / Крешков А.П. – М.:Химия, 1965. Т.1. – 498с.; Т.2. – 456с.
5. Барсукова З.А. Аналитическая химия / Барсукова З.А. – М.: Высш. шк., 1990. – 320с.
6. Крищенко В.П. Практикум по технике лабораторных работ / Крищенко В.П., Агеева В.С – М.:Агропромиздат, 1987. – 288с.
7. Крешков А.П. Безсеро-водородные методы качественного полумикроанализа / Крешков А.П., Мочалов К.Н., Михайленко Ю.Я. – М.: Высш. шк., 1979. – 271с.
8. Пономарев В.Д. Аналитическая химия (в двух частях) / Пономарев В.Д. – М.:Химия, 1991. – 846с.
9. Блок Н.И. Качественный химический анализ / Блок Н.И. – М. Госхимиздат, 1952. – 667с.
10. Скуг Д. Основы аналитической химии / Скуг Д., Уэст Д. – М.:Мир, 1979, Т.1. – 480с.; Т.2. – 438с.
11. Лайтинген Г.А. Химический анализ / Лайтинген Г.А. – М.:Химия, 1966. – 656с.
12. Гиллебранд В.Ф. Практическое руководство по неорганическому синтезу / Гиллебранд В.Ф., Лендель Г.З., Брайт Г.А., Гофман Д.И. – М.:Мир, 1967. – 1111с.

13. Посыпайко В.И. Химические методы анализа / Посыпайко В.И., Козырева Н.А., Логачева Ю.П. – М.: Высш. шк., 1989. – 448с.

14. Васильев В.П. Аналитическая химия. В 2-х ч. – Ч.1. – Гравиметрический и титриметрический методы анализа / Васильев В.П. – М.: Высш. шк., 1989. –320с.

15. Добжицкий Я. Химический анализ в сахарном производстве / Добжицкий Я. – М.:Пищевая промышленность, 1985. – 351с.

16. Кунце У. Основы качественного и количественного анализа / Кунце У., Шведт Г. М.: Мир, 1997. – 424с.

17. Бишоп Э. Индикаторы в 2 т / Э. Бишоп. - М.:Мир, 1976. Т. 1. - 384 с. Т. 2. – 460с.

18. Ушакова Н.Н. Курс аналитической химии для почвоведов / Ушакова Н.Н. - М.:МГУ, 1984. –349с.

19. Гороновский И.Т. Краткий справочник по химии / Гороновский И.Т., Назаренко Ю.П., Некряч Е.Ф. – К.: Наукова думка, 1987. – 829с.

20. Лурье Ю.Ю. Справочник по аналитической химии / Лурье Ю.Ю. – М.:Госхимиздат, 1962. – 672с.

21. Лурье И.С. Технохимический контроль сырья в кондитерском производстве: Справочник. / Лурье И.С. – М.:ВО „Агропромиздат„, 1987. – 272с.

22. Наместников А.Ф. Методы анализа пищевых, сельскохозяйственных продуктов и медицинских препаратов / Наместников А.Ф. – М.:Пищевая промышленность, 1974. – 743с.

23. Яцимирский К.Б. Константы нестойкости комплексных соединений / Яцимирский К.Б., Васильев В.И. – М.:Из-во АН СССР, 1959. – 230с.

24. Алимарин И.П. Справочные таблицы по аналитической химии / Алимарин И.П., Ушакова Н.Н. – М.: Из-во МГУ, 1960. – 389с.

25. Золотов Ю.А. Основы аналитической химии. В 2 кн. Кн. 2. Методы химического анализа. Учеб. для вузов. – 2-е изд., перераб. и доп. / Золотов Ю.А., Дорохова Е.Н., Фадеева В.И. – М.: Высш. шк., 2000. – 494с.
26. Золотов Ю.А. Основы аналитической химии. Практическое руководство / Золотов Ю.А. – М.: Высш. шк., 2001. – 464с.
27. Рабинович В.А. Краткий химический справочник / Рабинович В.А., Хавин З.Я. – СПБ.: Химия, 1992.- 376с.
28. Коренман Я.И. Практикум по аналитической химии. Анализ пищевых продуктов: В 4-х книгах. 2-е изд., перераб. и доп. Книга 1. Титриметрические методы анализа / Коренман Я.И. – М.:Колос, 2005. – 239с.
29. Шварценбах Г. Комплексонометрическое титрование: Пер. с нем. Шварценбах Г., Флашка Г. – М.:Химия, 1970. – 360с.
30. Kellner R. Analytical chemistry: a modern approach to analytical science / Kellner R., Wiley J. – 2004. - 1209 p.
31. Chan C. Analytical method validation and instrument performance verification / Chan C., Wiley J.– 2004. - 303 p.
32. Harvey D. Modern analytical chemistry / Harvey D. – 2000. - 816 p.

НАВЧАЛЬНЕ ВИДАННЯ

(виправлене та доповнене)

АНАЛІТИЧНА ХІМІЯ

(англійською мовою)

Укладачі:

ВОЙТЕНКО ЛАРИСА ВЛАДИСЛАВІВНА
КОСМАТИЙ ВОЛОДИМИР ЄВДОКИМОВИЧ
КОПІЛЕВИЧ ВОЛОДИМИР АБРАМОВИЧ
ЛАВРИК РУСЛАН ВОЛОДИМИРОВИЧ

Навчальний посібник

Рекомендовано
Міністерством освіти і науки України як навчальний посібник для студентів вищих навчальних закладів (лист №1/ІІ-688 від 10.02.2010 р.)
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