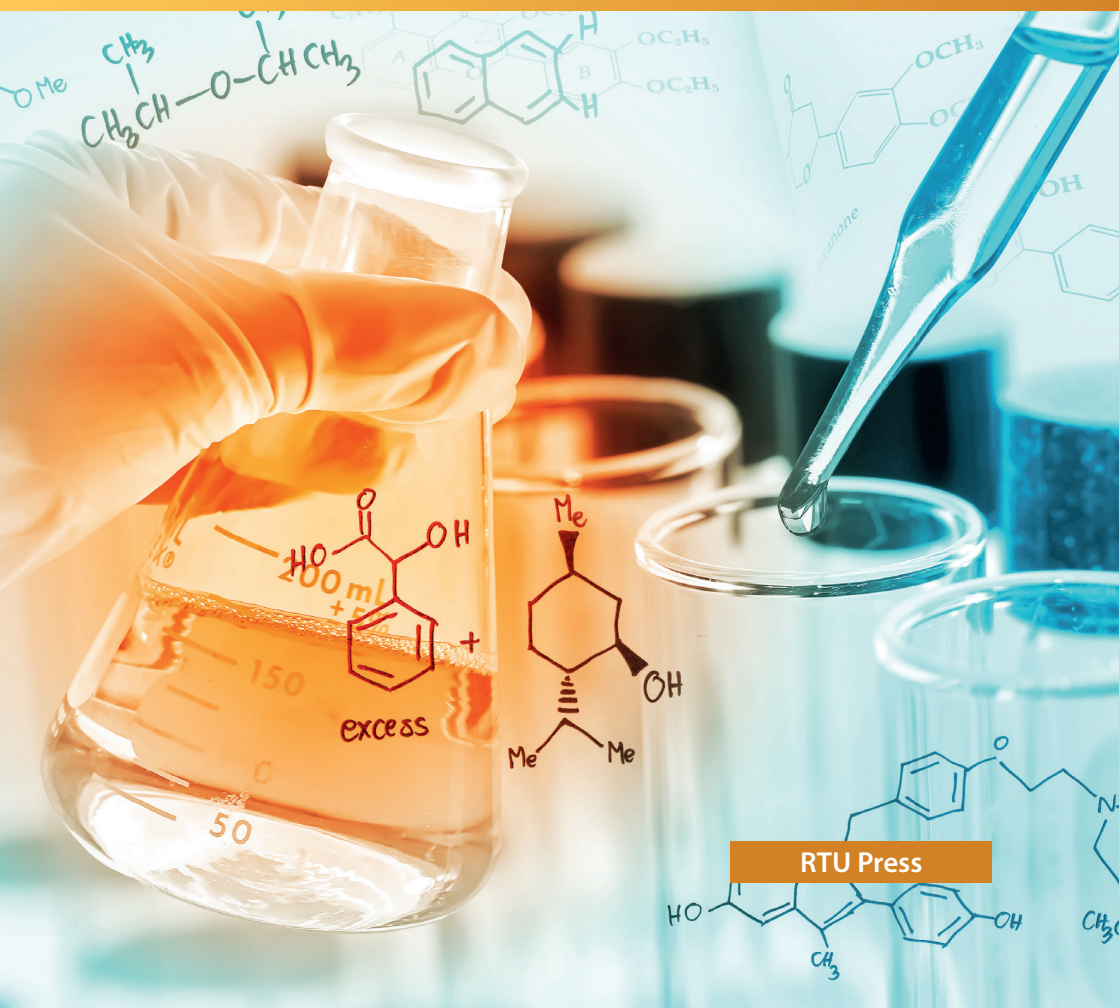


Jānis Putniņš

SELECTIVE QUALITATIVE ANALYSIS



Riga Technical University
Faculty of Materials Science and Applied Chemistry
Institute of Applied Chemistry
Department of Chemistry

Jānis Putniņš

**SELECTIVE
QUALITATIVE ANALYSIS**

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This teaching aid describes selective microanalysis and semi-microanalysis methods for detection of 50 different cations and anions as well as the qualitative analysis of waste water. It is intended for students of chemistry and chemical engineering programmes at the Faculty of Materials Science and Applied Chemistry, Riga Technical University.

Translated by Ēriks Pālītis

Editor Zilgma Irbe

Computer Designer Baiba Puriņa

Cover Designer Baiba Lazdiņa

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Qualitative chemical analysis is divided into systematic and selective.

In the course of **systematic analysis**, components (ions) of the test solution first are separated into certain groups. Then the separation continues within each group, and, only when one kind of ions is left in the solution or the sediment, they are identified. This method was created at the end of the 18th century by Swedish chemist T. Bergman. Formally it is very simple, does not require deep knowledge of chemistry but only a thorough job. The main drawbacks of systematic analysis are its labour intensity, duration and larger or smaller analyte loss because of numerous separation operations.

Systematic analysis methods, which for many decades were mainly used for instruction in laboratories, lately gradually lose their dominant role. Instead, the so-called **selective analysis** of individual components is starting to be used more often. In selective analysis the individual components of the test sample are usually identified in an arbitrary order using selective reagents and by creating the right conditions for maximum elimination of interference of other ions. Selective analysis is particularly useful in those cases where the presence of certain components in the analyzed object has to be clarified (as it is most often in practice). Such methods were more broadly developed in the first half of the last century in the works N. Tananaev and F. Faigl. They systematized the existing methods and created new, simple microanalysis methods (mainly the so-called drop analysis) to identify a number of ions.

Selective analysis uses new selective organic reagents and simple separation operations (extraction, paper chromatography, volatilization). Selective analysis is currently widely used not only to solve practical problems but also is successfully implemented in academic laboratories.

This teaching aid describes the methods of identification of 50 most common cations and anions. Material in the teaching aid is arranged according to the practical training program in qualitative analysis. In the program students of chemical engineering have to complete five

laboratory modules. In the first module the students are acquainted with analysis of mixture of cations, in the second — with anion analysis, in the third — with detecting some of the so-called rare elements, and in the fourth and fifth modules analysis of two real objects is performed. In the fourth and fifth modules the identification of presence of harmful impurities in waste water and the identification of the main components of a solid object (a mixture of substances, an alloy etc.) is shown.

Mostly microanalysis methods are recommended. Microanalysis methods are performed in a test tube, in a cavity of a drop plate or on a filter paper. Several ions can be detected using specially prepared reagent papers; this gives the opportunity to accelerate the analytical procedure and to save reagents. Some ions are identified after their prior chromatographic separation on paper.

From a great number of methods described in literature, relatively simple and fast but at the same time sufficiently selective and sensitive methods were included in this book. Most of these methods have been used in laboratory practice for many years and are well-tested, and the conditions of implementation of these methods are repeatedly specified.

Due to the limited number of pages in this teaching aid, **analysis of solid objects** is described only as a general guide.

1. ANALYSIS OF CATIONS

This section describes simple or combination methods of selective detection of 25 frequently occurring cations:

Ag^+ , Hg^{2+} , Hg_2^{2+} , Pb^{2+} , Bi^{3+} , Cu^{2+} , Cd^{2+} , Sn(II, IV) , Sb(III) , As(III, V) , Co^{2+} , Ni^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Zn^{2+} , Cr^{3+} , Al^{3+} , Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and NH_4^+ .

With these methods the listed cations can only be detected if no interfering anions are present. The test solution may only contain nitrate, chloride, sulfate, and carbonate anions. Other anions have to be removed (see page 63, Chapter 5).

Simple selective analytical methods are usually taken to be such if they can detect the target ion in the presence of all other ions (by creating a certain environment for the reaction and by adding reagents that mask the interfering ions).

In combined selective analytical methods the ion to be identified is first separated from most of the other ions by precipitation of a small group of ions that includes the ion to be identified. The precipitate is then dissolved, and the target ion is detected in the resulting solution using appropriate reagents.

To detect the presence of all of the abovementioned ions about 2 cm^3 of the test solution is necessary if the ion concentration in the solution is about $0.01 \dots 0.05 \text{ mol/dm}^3$.

The sequence in which individual cations are detected in the course of selective analysis is not of great importance. Identification of some ions is described in more than one selective method. First, the quickest and easiest methods are described. But, if the presence of other ions interferes with reliable results, then it is necessary to use methods described afterwards.

Before identification of separate ions, it is useful to perform some simple preliminary tests. This often makes it possible to shorten and to accelerate the analytical procedure.

1.1. Preliminary tests

1. **pH test.** Place a drop of the test solution on a universal pH indicator paper using a dropper or a glass rod. pH of the solution is determined by immediately comparing the resulting coloured spot with colour scale.

If the pH of the test solution is ≤ 1 , a drop of the test solution can be additionally placed on a methyl violet paper. If $\text{pH} \sim 0.5$, the coloured spot on the paper appears green; if $\text{pH} < 0.1$, the coloured spot is yellow.

If the test solution is clear (free from sediment and turbidity) and its $\text{pH} \sim 4$, then such solution cannot contain Bi^{3+} , Sb^{3+} , Hg_2^{2+} or Sn(II, IV) . If the test solution is clear and its $\text{pH} \sim 6$, then significant quantities of Fe^{3+} , Cr^{3+} or Al^{3+} also cannot be present. If it is so, there is no need to test the presence of these ions.

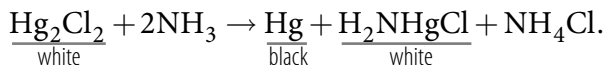
2. **Precipitation of sulfides.** Place 2 drops of 0.5 M Na_2S solution in a conical test tube, add 2 drops of 2 M HCl solution, and mix using a rod. Then add a drop of neutral or moderately acidic test solution and mix again. If black or dark brown precipitate does not form, the test solution does not contain Ag^+ , Hg^{2+} , Hg_2^{2+} , Pb^{2+} , Cu^{2+} , and Bi^{3+} . But, if yellow or light brown precipitate does not form, Cd^{2+} , Sn(IV) or As(III) are also not present.

If sulfides are not precipitated from the acidified test solution, continue the test by adding 6 M NH_3 solution to the test tube until pH is 10. If no black precipitate forms in the ammoniacal environment, Co^{2+} , Ni^{2+} , Fe^{2+} or Fe^{3+} ions are not present in the test solution.

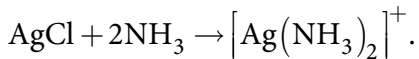
1.2. Detection of Ag^+ and Hg_2^{2+}

Place 2 drops of the test solution (or stirred suspension if the test solution contains precipitates) in a conical test tube, add 2 drops of 6 M HCl solution and heat in a water bath. If precipitate (which may be AgCl or Hg_2Cl_2) is present (or remains), the test solution has to be centrifuged. The supernatant is not required for further analysis. Wash the precipitate with 2 cm^3 of distilled water while heating in a water bath and stirring. Add a drop of 25 % NH_3 solution to the washed precipitate and mix.

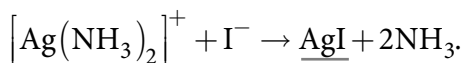
In the presence of mercury(I) ions, the precipitate becomes black:



But, if the sediment contains only AgCl, it is completely dissolved:

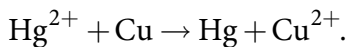


If the resulting precipitate is black, it must be centrifuged. Place a drop of the clear solution with ammonia in a conical test tube or on a glass slide, add a drop of 10 % KI solution. In the presence of silver ions yellow precipitate forms:



1.3. Detection of Hg^{2+} and Hg_2^{2+}

Place a small drop of the test solution on a clean copper plate using a dropper. After 5 min dry the plate by lightly rubbing it with a strip of filter paper. If the test solution contains mercury ions, a bright mirrored spot can be observed on the plate — copper amalgam:



pC = 3.7.

To observe how a spot resulting from the presence of mercury ions must look, place a small drop of 0.01 M $\text{Hg}(\text{NO}_3)_2$ solution next to the droplet of test solution.

If the test solution contains chloride ions, Hg_2^{2+} ions may be precipitated as poorly soluble Hg_2Cl_2 that does not react with the copper plate.

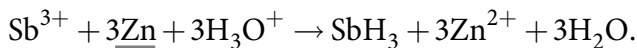
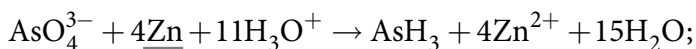
1.4. Detection of As(III) and Sb(III, V)

Arsenic and antimony compounds are easily detected using a Zangger-Black's apparatus, which consists of 10...20 cm³ bottles or test tubes and a specialized stopper (Fig. 1).

In the widest part of the specialized stopper place a crimped lead acetate paper; the lead acetate paper binds hydrogen sulfide which can be released during the analysis if some sulfur compounds are present. This paper should only be replaced with a new one if it has become halfway black or brownish.

At each test procedure a new HgCl₂ or HgBr₂ paper should be placed in the thin upper tube of the specialized stopper.

When the specialized stopper is arranged for the test, place 2 drops of the test solution (or suspension) in a carefully washed bottle (or a test tube) and add 1 cm³ of 0.01 M SnCl₂ solution in 6 M HCl, then add a zinc pellet (~0.5 g), and immediately cover with the specialized stopper. If the test solution contains arsenic or antimony compounds, they are reduced to AsH₃ and SbH₃:



Arsine and stibine are released and react with the mercury(II) halide paper forming coloured compounds, such as: AsH₂(HgCl), AsH(HgCl)₂, As(HgCl)₃, As₂Hg₃, Sb₂Hg₃ etc. These arsenic compounds are yellow or brown, but antimony compounds — black.

If the concentration of arsenic and antimony compounds in the test solution is high, the reagent paper colours faster. If the colour does not appear within 30 min, it can be concluded that these compounds are not present in the test solution in any considerable amount.

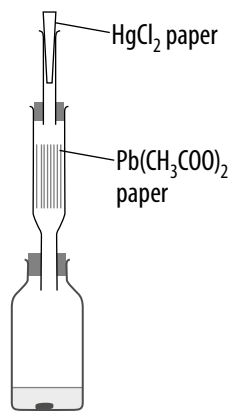


Fig. 1. Zangger-Black's apparatus for detection of arsenic and antimony.

Sensitivity of the reactions: $pC = 4$ (As); $pC = 3$ (Sb).

If the test solution simultaneously contains both arsenic and antimony compounds, they are quite difficult to verify because of each other.

The sensitivity of the reaction is greatly reduced by the presence of mercury ions and, to a lesser extent, the presence of lead, silver, bismuth, and even iron, cobalt, and manganese ions, if their concentration is high.

1.5. Detection of Sn(II, IV)

Place a drop of the test solution (or stirred suspension if the test solution contains precipitate) in a porcelain crucible, add 15 drops of 6 M HCl solution and a zinc pellet (~0.5 g). Stir the contents of the crucible with a 15 cm³ test tube filled with cold water. Place the moist tip of the test tube in the colourless outer part of a gas flame, as shown in Fig. 2.

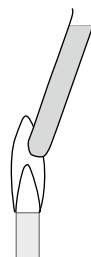


Fig. 2. Detection of tin ions.

In the presence tin ions quickly fading bluish flames appear after a few seconds on the walls of the wetted test tube.

The reaction mechanism is not known precisely. It may be that SnHCl_3 is formed, which then decomposes in the flame giving it the characteristic colour.

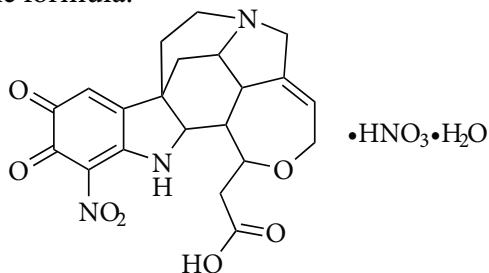
The reaction is quite specific (only gold ions can interfere with the detection), but it also has relatively low sensitivity ($pC = 4$).

1.6. Detection of Sn^{2+} , Bi^{3+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Hg^{2+} , Co^{2+} , and Ni^{2+}

Place a drop of the test solution (or stirred suspension if the test solution contains precipitate) in a conical test tube, add a drop of 1 M ZnSO_4 in 4 M HCl solution, mix with a glass rod, and heat for 5 min in a water bath. Place small amounts of the acidified solution on the following reagent papers using a capillary dropper and observe the formation of characteristic coloured spots. Then make conclusions about the detected ions:

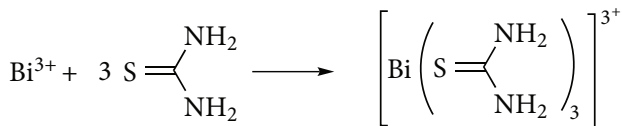
- if a violet spot forms on a **cacotheline** paper, the solution contains tin(II) ions which reduce cacotheline (pC = 4).

Cacotheline formula:



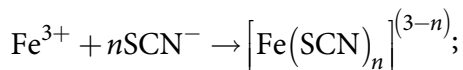
A similar reaction occurs in the presence of other strong reducing agents (H₂S, S₂O₄²⁻, Cr²⁺, Ti³⁺, Cu⁺);

- if a bright yellow spot forms on a **thiocarbamide** paper, the test solution contains bismuth(III) ions (pC = 5):

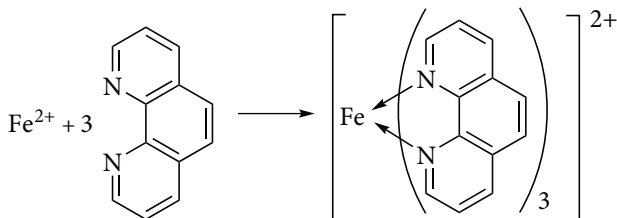


Presence of Sb(III) ions results in a pale yellow spot, so the presence of small quantities of bismuth ions cannot be detected;

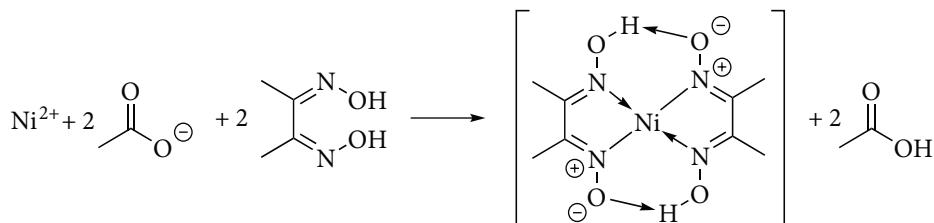
- if a reddish brown spot that gradually fades forms on a **thiocyanate** paper, the test solution contains iron(III) ions (pC = 5.4):



- if a orange-red spot or ring forms on a **o-phenanthroline** paper, the test solution contains iron(II) ions (pC = 5):



- if a pink spot or ring forms on a **diacetyldioxime** paper, the test solution contains nickel ions (pC ~ 5):



If the test solution contains copper or cobalt ions besides nickel ions, the spot is brownish-pink;

- if a bright blue spot forms on a **tetrarodanomercurate** paper, the solution contains cobalt ions (pC = 4.5). If a dirty violet spot forms, the solution contains copper ions (pC = 4.5).

Mixed salts $(\text{Zn},\text{Co})[\text{Hg}(\text{SCN})_4]$ and $(\text{Zn},\text{Cu})[\text{Hg}(\text{SCN})_4]$ are formed.

If the test solution contains both copper and cobalt ions, the spot on the reagent paper is dirty dark blue. In this case it is more appropriate to separate both ions by chromatography and detect them using dithiooxamide (see below).

If the solution contains iron(III) ions, the resulting spot on the tetrarodanomercurate paper is reddish at first, but then it gradually disappears and is replaced by a light blue or violet tint. If iron(III) concentration is large and the reddish colour disappears slowly or incompletely, it is preferred to moisten the coloured spot with saturated NaF solution.

If the test solution contains tin(II) or iron(II) ions, the tetrarodanomercurate paper test does not give reliable results. In this case it is recommended to make a test on an iodide paper (see below). But afterwards add a drop of 10% H_2O_2 solution to the conical test tube containing the remaining solution and heat for 10 min in a water bath to oxidize tin(II) and iron(II) ions. Following that, place a drop of the solution on a tetrarodanomercurate paper again;

- on an **iodide** paper after 3...5 min concentrically arranged coloured bands appear (from the centre of the spot to the periphery): reddish orange (HgI_2) — in the presence of mercury ions, black or gray (BiI_3) — in the presence of bismuth ions, brown (I_2) — in the presence of copper or iron(III) ions, which oxidize iodide ions to free iodine.

1.7. Detection of Cu^{2+} , Ni^{2+} , Co^{2+} , and Cd^{2+}

Place 3 drops of test solution (if the solution is cloudy then the drops should also contain the precipitate!) in a conical test tube, add 3 drops of 25% NH_3 solution, and mix thoroughly with a glass rod for a few minutes. Centrifuge. Transfer the clear supernatant to a small porcelain crucible, add 5 drops of 37% HCl solution, gently evaporate to dryness on a hotplate. Heat the dry residue on a gas flame until white smoke is no longer produced (ammonium salts). Cool the crucible, add a drop of 37% HCl solution, and mix. Copper, nickel, cobalt, and cadmium ions in the resulting solution (A) are separated using chromatography and identified.

1. Place small drops of the solution (see above) using a capillary dropper on the starting line of 55 mm long filter paper strips cut specifically for this purpose (see Fig. 3).

The wet spots should have a diameter no larger than 5 mm; the strips should be carefully dried over a hotplate, and small drops of solution A

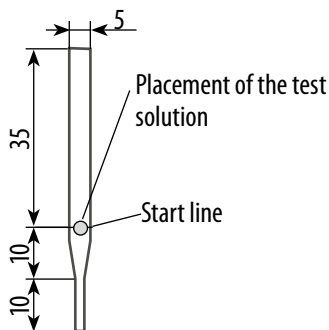


Fig. 3. Filter paper strip for chromatography.

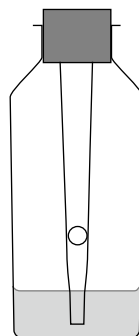


Fig. 4. Chromatography bottle.

should be placed at the same place repeatedly and dried again. Filter paper strips prepared in such way should be mounted in the slit of a rubber stopper, as shown in Fig. 4.

Add 2 cm³ of butanol saturated with 3 M HCl solution to a dry 15 cm³ chromatography bottle. Close the bottle with a stopper mounted with the prepared filter paper strip; the strip should be placed no deeper than 10 mm in the eluent. While the chromatography proceeds (process time ~20 min), the bottle should not be moved!

When the hydrochloric acid solution in butanol is absorbed through the filter paper strip almost to the stopper (it is better, if a wet border can be seen by looking up to the light), stop the chromatography and immediately note the line up to which the solution was absorbed (the finish line) a graphite pencil. Then carefully dry the strip over a hot stove. Pour 3 % Na₂S solution into a flat Petri dish and immerse the dried filter paper strip in it for 30 seconds. If the test solution contains cadmium ions, a light yellow CdS band forms on the filter paper strip about midway between the start and finish lines.

2. Place a small drop of test solution A (see above) using a capillary dropper on the starting line of a 55 mm long filter paper strip cut specifically for this purpose (see Fig. 3). The diameter of the wet spot must not exceed 4...5 mm. Carefully dry the filter paper strip over a hotplate. Then, if concentration of analyte is low, repeatedly place small drops of the solution at the same place and dry again. Mount the prepared filter paper strip in the slit of a rubber stopper (see Fig. 4). Pour 1 cm³ of mixture of acetone and 20 % HCl solution (88:12) in a dry chromatography bottle (15 cm³). Plug the bottle with the stopper (with the prepared chromatography filter paper strip fixed in it), then sink the strip of filter paper in the solution (eluent) but no deeper than 10 mm. During the chromatography process the bottle must not be moved.

When HCl-acetone solution is absorbed by the filter paper strip almost to the stopper (the level of eluent can be better observed by looking up to the light), the chromatography is finished. Immediately note the finish line to which the solution was absorbed with a graphite pencil.

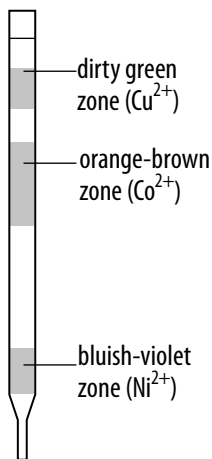


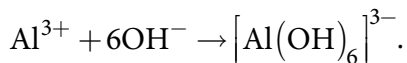
Fig. 5. Chromatogram.

Dry the filter paper strip carefully over a hotplate. Then moisten the zone between the start and finish lines with saturated solution of dithiooxamide in ethanol using a dropper and hold the strip above an open bottle of 25 % NH_3 solution.

In the ammoniacal environment the characteristic colours of copper, cobalt, and nickel dithiooxamides appear (corresponding colours — dirty green, orange brown, and bluish violet); these are located on the chromatogram as shown in the example in Fig. 5.

1.8. Detection of Al^{3+}

Place a drop of the test solution in a conical test tube, add 1 drop of 6 M NaOH solution, a drop of 1 M Na_2CO_3 solution, and mix with a glass rod. Most of the ions are precipitated as hydroxides or carbonates under such conditions, but aluminium ions remain in solution in the form of hydroxo complex:

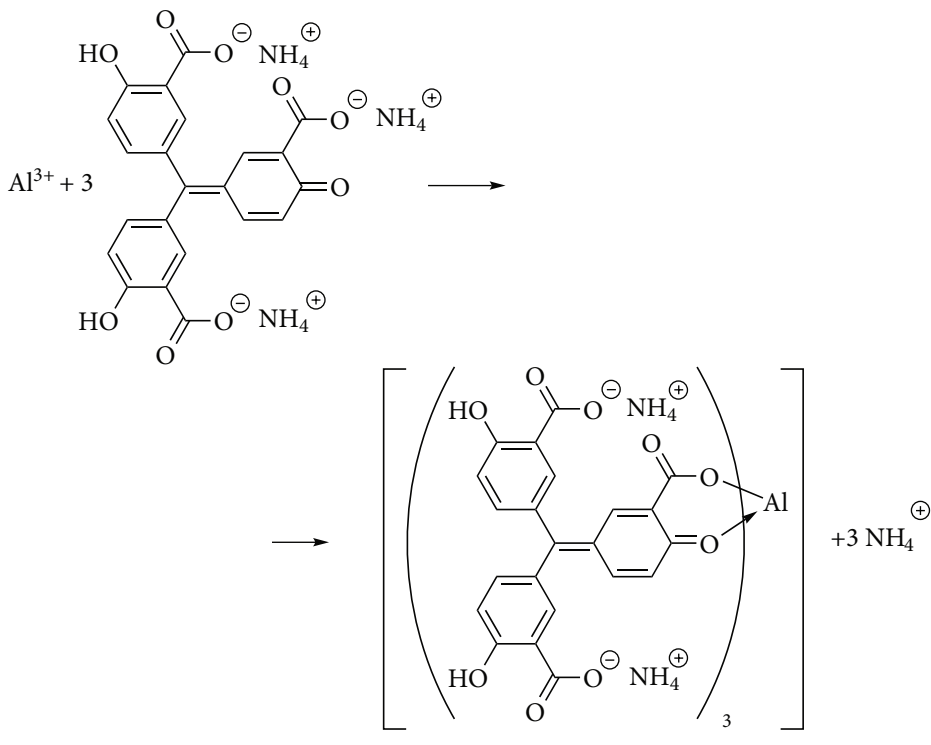


Centrifuge. Pour the supernatant into a 10...15 cm^3 test tube and dilute with distilled water to 5 cm^3 . At the same time do a control test by placing 5 cm^3 of distilled water in a second test tube of the same size. Add a drop of 37 % HCl solution and 2 drops of 10 % ascorbic acid solution in both test tubes, swirl. After a few minutes add 1 drop of 1 % phenolphthalein solution to both test tubes, then add 5 % NH_3 solution drop by drop while shaking the test tube until a pink hue appears. Then add 8 drops of 6 M $\text{CH}_3\text{COONH}_4$ solution and 2 drops of 6 M HCl solution. Mix. The pink colour should disappear. If the colour does not disappear (this indicates that too much ammonia has been added because of insufficient mixing), add a few more drops of 6 M HCl solution. Then add three drops of 0.2 % aluminon solution to the bleached solutions in

both test tubes. If the test solution is significantly redder than the blank solution after 10 minutes have passed, it can be concluded that the tested solution contains aluminium ions.

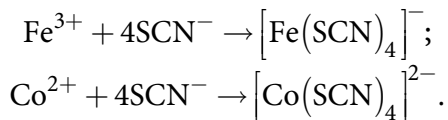
$pC = 5.7$.

It is thought that the following reaction occurs:



1.9. Detection of Fe^{3+} and Co^{2+}

Place one drop of the test solution in a cavity of a drop plate, add 3 drops of 20% KSCN solution and a few drops of acetone, and mix with a glass rod. Iron(III) ions produce red and cobalt ions produce blue (sometimes greenish) thiocyanate complexes, such as:

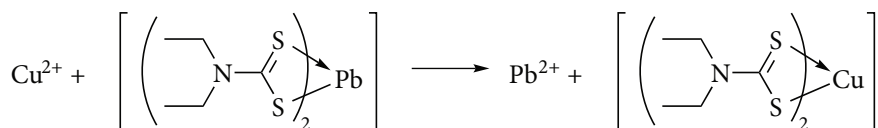


In the presence of iron(III) it is difficult to detect Co(II) ions because the red colour normally covers the blue colour. In this case add a small amount of crystalline NaF and mix with a glass rod. $[\text{Fe}(\text{SCN})_4]^-$ ions turn into colourless $[\text{FeF}_6]^{3-}$ ions; therefore, it is no longer an obstacle to see the blue colour of $[\text{Co}(\text{SCN})_4]^{2-}$.

Larger quantities of Cu^{2+} interfere with the analysis because black $\text{Cu}(\text{SCN})_2$ forms.

1.10. Detection of Cu^{2+}

Take a test tube (10...15 cm³) and add a drop of the test solution, 5 cm³ of distilled water, a drop of 40 % ammonium citrate solution, 2 drops of 0.1 M complexone III solution, and 0.5 cm³ of lead **diethyldithiocarbamate** solution in carbon tetrachloride. Close the test tube with a polyethylene stopper and shake vigorously. In the presence of copper ions the lower layer of carbon tetrachloride becomes tan:



Bi^{3+} ions interfere with the test.

1.11. Detection of Zn^{2+} , Pb^{2+} , and Al^{3+}

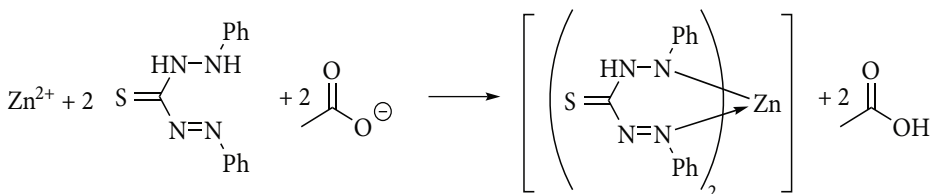
Place 5 drops of the test solution in a conical test tube. Then (while stirring with a glass rod) add 0.5 M Na_2HPO_4 solution until new precipitate no longer appears. If the test solution is not very acidic, usually 6...8 drops of phosphate solution are sufficient. Centrifuge. Discard the supernatant. Wash the phosphate precipitate with 1 cm³ of distilled water. Add about 10 drops of 2 M NaOH solution to the washed precipitate and stir for about 2 min. Zinc, lead, and aluminium phosphates are dissolved. If there still is some precipitate — centrifuge. After the separation of the precipitate add a drop of 1 % phenolphthalein solution in ethanol to the supernatant and then while stirring add 6 M HNO_3 drop by drop until the pink colour of phenolphthalein disappears. If precipitate has appeared after the acidification, add an extra drop of nitric acid and heat in

a water bath until the precipitate dissolves. Use the resulting solution (A) for detection of zinc, lead, and aluminium ions.

1. Place a drop of solution A in a cavity of a drop plate, then add a drop of 0.02 % CoCl_2 solution, a drop of $\text{K}_2[\text{Hg}(\text{SCN})_4]$ solution, and mix with a glass rod (see page 13, Section 1.6). In the presence of zinc ions light blue $(\text{Zn}, \text{Co})[\text{Hg}(\text{SCN})_4]$ precipitate forms.

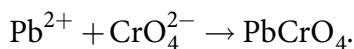
If in the presence of iron(III) ions red colouration that makes it difficult to see the blue precipitate appears, add a drop of saturated NaF solution and mix. The red colour disappears because colourless $[\text{FeF}_6]^{3-}$ ions form.

2. Place 5 drops of solution A in a conical test tube, add 5 drops of acetate buffer ($\text{pH } 4, \mu = 2$), and mix. Then using a universal pH indicator paper verify that the solution has a pH between 4...5 (if necessary, add a few more drops of the buffer). Then add 10 drops of 25 % $\text{Na}_2\text{S}_2\text{O}_3$ solution and 30 drops of 0.01 % dithizone solution in carbon tetrachloride. Close the test tube with a polyethylene stopper and shake vigorously for about a minute. In the presence of zinc ions the CCl_4 layer becomes pink:



$\text{pC} = 3.8$.

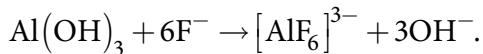
3. Place 5 drops of solution A in a conical test tube, add 2 drops of acetate buffer solution and a drop of 10 % K_2CrO_4 solution. In the presence of lead ions yellow precipitate forms:



$\text{pC} = 4.5$.

4. To the remaining part of solution A add one more drop of phenolphthalein solution, and then while stirring carefully add 0.5 M NaOH solution drop by drop until pink colour appears again. Then while gently

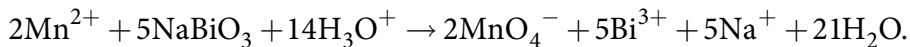
stirring add 0.1 M HCl solution drop by drop until the colour of phenolphthalein disappears. Under these conditions aluminium ions in the solution form $\text{Al}(\text{OH})_3$. Then add 10 drops of saturated NaF solution. If the aluminium hydroxide was previously formed, it slowly reacts with fluoride ions to form stable fluoride complexes and to release hydroxyl ions, which re-establish the pink colour of phenolphthalein:



Attempt usually proceeds well if by stirring carefully the addition of HCl and NaOH solutions in excess is avoided. Excess of HCl greatly reduces the sensitivity of the reaction.

1.12. Detection of Mn^{2+}

Place one drop of the test solution in a cavity of a drop plate, add a drop of 6 M HNO_3 solution and ~15 mg of NaBiO_3 . In the presence of manganese ions the solution turns pink or violet:



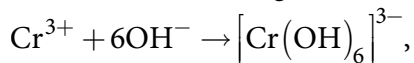
pC = 4.7.

In the presence of tin(II), iron(II), arsenic(III) and some other reducing ions, the violet colour appears after a moment.

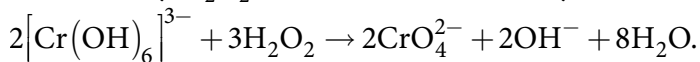
Sometimes it is necessary to add more NaBiO_3 . The reaction can be impeded by the presence of high amounts of chloride ions or by the presence of manganese(II) ions themselves in large concentrations. In such cases the detection often is more successful, if the test solution is diluted with water by about ten times.

1.13. Detection of Cr^{3+}

1. Place a drop of the test solution into a conical test tube, add 2 drops of 6 M NaOH solution and 3 drops of 10% H_2O_2 solution. Heat the conical test tube for 5 min in a water bath. In alkaline environment chromium(III) ions form chromite ions (green):



which are oxidized by H_2O_2 to form chromate ions (yellow):



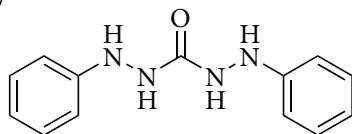
Centrifuge the solution. In the presence of chromium ions the clear supernatant is yellow or green-yellow (yellow precipitate does not indicate the presence of chromium).

$$\text{pC} = 4.$$

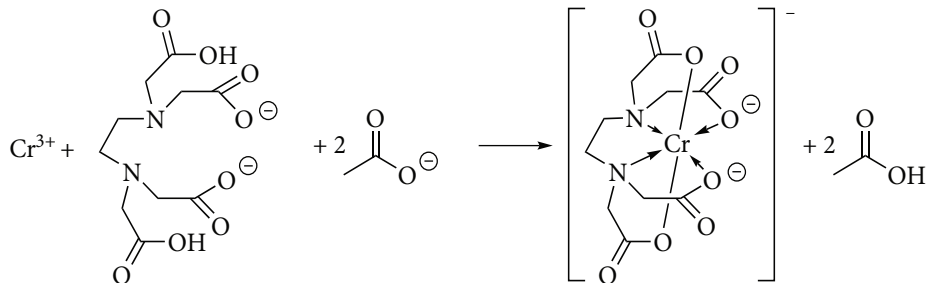
In the presence of manganese, cobalt, and nickel ions, the sensitivity of the reaction decreases.

A remark. If the yellow colour of the supernatant is uncertain, it is recommended to heat the test tube with the solution in a water bath for additional 10...15 min to completely decompose the excess of added hydrogen peroxide. Then transfer only one (!) drop of the solution into another test tube and add 2...3 mL of distilled water, 1 drop 6 M H_2SO_4 solution, and a few drops diphenylcarbazide solution. In the presence of chromate ions (that form by oxidation of chromium(III) ions) the solution gradually acquires reddish violet hue.

Formula of diphenylcarbazide:



2. Place a drop of the test solution into a conical test tube, add a drop of 6 M $\text{CH}_3\text{COONH}_4$ solution, 3 drops of saturated complexone III solution, and heat in a water bath for a few minutes. In the presence of chromium ions violet complexonate is formed:



Under the described conditions some other colourful complexonates also form. For example, copper and nickel complexonates are blue, cobalt complexonate — pink, and iron(III) complexonate — yellow. In the presence of these ions the detection of chromium(III) is difficult. If the test solution contains copper (or nickel) and cobalt ions at the same time, the colour of such complexonate mixture can be quite similar to the colour of chromium(III) complexonate.

1.14. Detection of Pb^{2+} , Ba^{2+} , Sr^{2+} , and Ca^{2+}

Separation and detection of these ions is shown below.

To 2 drops of test solution (or suspension, if the solution is cloudy) in a conical tube add a drop of 2 M H_2SO_4 solution and mix. If mercury(I) ions are found in the solution, before acid addition add a drop of 10 % H_2O_2 solution and heat for 5 min on a water bath. If precipitation occurs (or the existing precipitate does not dissolve) — centrifuge.

In supernatant: Ca^{2+} ions and many other ions.

Place a small drop of the supernatant on one end of a microscope slide. Hold the slide by the opposite end and very slowly evaporate the drop over a hot plate. The slide should be held ~ 1 cm away from the hot plate. Evaporate until the drop acquires a white border. But do not evaporate to complete dryness! In the presence of calcium ions, long needle-shaped $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals form on the slide. Observe these crystals under a microscope (Fig. 6).

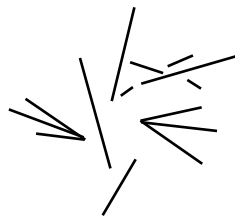
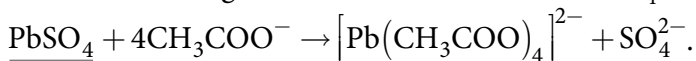


Fig. 6. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals.

Precipitate: PbSO_4 , BaSO_4 , SrSO_4 .

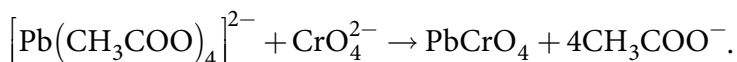
After the removal of the supernatant wash the precipitate twice with 1 cm³ of distilled water. Add 3 drops of 6 M $\text{CH}_3\text{COONH}_4$ to the washed precipitate and while heating in a water bath stir 2...3 min with a glass rod. If the sediment is PbSO_4 , it dissolves:



If the sediment does not dissolve, centrifuge it.

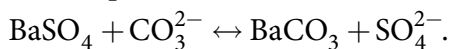
In supernatant: $[\text{Pb}(\text{CH}_3\text{COO})_4]^{2-}$.

Place a drop of the supernatant on a glass slide and add a drop of 10 % K_2CrO_4 solution. In the presence of lead ions yellow precipitate — PbCrO_4 — forms:



Precipitate: BaSO₄, SrSO₄.

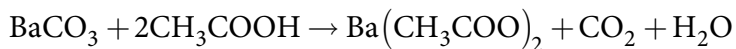
Wash the precipitate with 30 drops of distilled water. Add 10 drops of 1 M Na₂CO₃ solution to the washed precipitate and stir while heating in a water bath for about 10 min. Centrifuge. Discard the supernatant, treat the precipitate with 5 drops of Na₂CO₃ solution as indicated above. Such treatment turns barium and strontium sulfates into carbonates, for example:



Centrifuge again and discard the supernatant.

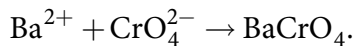
Precipitate: BaCO₃, SrCO₃.

After the removal of the supernatant, wash the precipitate with distilled water (1 cm³) and add 1 drop of 6 M CH₃COOH solution. The precipitate dissolves, for example:



In solution: Ba²⁺, Sr²⁺.

To the solution acidified by acetic acid add 1 drop 10 % K₂CrO₄ solution. The presence of barium ions results in yellow precipitate — BaCrO₄:

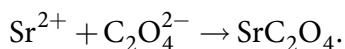


Centrifuge.

Precipitate: BaCrO₄.

In solution: Sr²⁺.

Add a drop of saturated (NH₄)₂C₂O₄ solution and 1 drop of 6 M NH₃ solution to the clear, yellow supernatant. In the presence of strontium ions, white precipitate forms immediately or after a few minutes:



1.15. Detection of Mg^{2+}

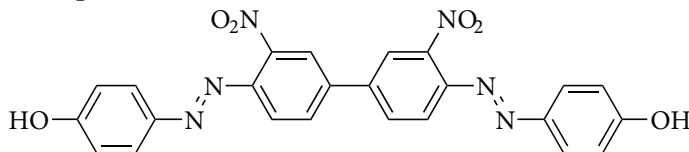
Place a drop of acidic test solution (preferably without residue) in a conical test tube, add 2...3 drops of 2 M NH_4Cl solution, 1 drop of 1 M Na_2CO_3 solution, and 1 drop of 0.5 M Na_2S solution. Mix. Most of the metal ions are precipitated under these conditions as sulfides, hydroxides or carbonates, but magnesium ions remain in the solution. Centrifuge.

Transfer the clear supernatant to another test tube, add 2...3 cm^3 of distilled water, a drop of 0.1 % phenazo solution, and 2 drops of 6 M NaOH solution. Mix. In the presence of magnesium ions the magnesium hydroxide precipitates in a strongly alkaline solution; the azo dyes are adsorbed on its surface. The precipitate is violet. If the amount of solid phase is low, the precipitate remains in a colloidal state, so the whole solution becomes violet.

$$pC = 4.$$

Pure phenazo reagent is orange red in an alkaline solution.

Formula of phenazo:



1.16. Detection of NH_4^+

Place a drop of the test solution in a porcelain crucible (volume $\sim 5\text{ cm}^3$), add 3 drops of 6 M NaOH solution, and immediately cover the crucible using a glass slide on the underside of which a small drop of Nessler's reagent is suspended (see Fig. 7).

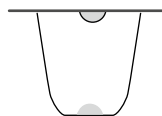
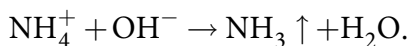


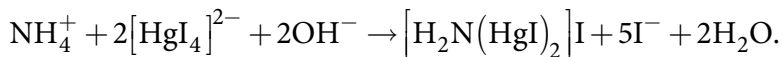
Fig. 7. Detection of NH_4^+ .

If the test solution contains ammonium ions, ammonia is released:



Ammonia in the presence of the Nessler's reagent forms either brown (reddish) precipitate ($pC = 4.5$) or just orange (yellow) colouring ($pC = 6.5$). The composition of the coloured compounds is variable and

depends on the ratio of the reactants, for example:



As the laboratory air and the reagents used in the test usually contain small quantities of ammonia and ammonium salts, yellow or even orange colouring almost always occurs. The presence of a considerable amount of ammonium ions in the test solution can be attested only if the brown precipitate forms.

Ammonia released from the alkaline test solution can also be detected by the characteristic odour or using a pH indicator. In this case, affix a pH indicator paper moistened with distilled water to the bottom of the slide instead of the drop of Nessler's reagent. Ammonia causes the red litmus paper to colour blue, the colourless phenolphthalein paper to colour red, the colourless thymolphthalein paper to colour blue, the yellow universal pH indicator paper — green or gray violet etc. In order to avoid erroneous conclusions, ensure that the pH indicator paper does not come into contact with the alkaline solution in the crucible. Therefore, the glass slide which covers the crucible must be dry and the paper moistened only enough to stick to the glass slide.

1.17. Detection of Na^+

Almost all sodium salts have good solubility, so sodium ions usually are not found in the precipitate. If the test solution is cloudy, then place one drop of the solution in a conical test tube, centrifuge, and use the obtained supernatant to test for sodium ions.

1. Place a small drop of the clear test solution on a glass slide. Adjacent to the small drop of test solution, place a small drop of mixture of zinc and uranyl acetate solutions. Using a thin and dry glass rod make a narrow channel between the two drops of the solutions, thus allowing the reactive substances to slowly mix. If the test solution contains sodium ions, relatively large

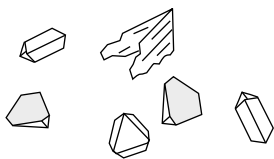


Fig. 8. $\text{NaZn}(\text{UO}_2)_3(\text{CH}_3\text{COO})_9 \cdot 6\text{H}_2\text{O}$ crystals.

crystals that sparkle and have the characteristic polyhedron shape are formed. These crystals should be observed using a microscope (Fig. 8).

$$pC = 4.7.$$

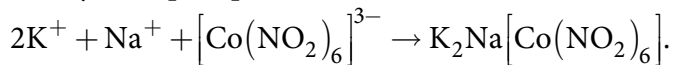
2. Place a small drop of the test solution on a clean nichrome wire loop using a dropper and place the wire loop in the colourless part of a gas flame. In the presence of sodium compounds, the flame colours intensely yellow. The colour appears even if only 10^{-10} g of sodium ions are present. If sodium ions are present in significant quantities, the colour is not only intense but remains visible for at least 10–20 s.

Using this mode of detection, one must learn to distinguish between the colour of flame caused by sodium and the brick red colour of flame that appears in the presence of calcium ions. In addition, it must be taken into account that a short and rather bright, yellow flame results from the decomposition of ammonium salts. Also, a few organic substances produce a relatively lengthy colouring of the flame while burning.

1.18. Detection of K^+

1. Place 2 drops of the test solution into a conical test tube, add a drop of 0.5 M NaCl solution, and while stirring with a glass rod add 1 M Na_2CO_3 until pH 10 is achieved (control using a universal pH indicator paper). If precipitate forms, centrifuge. The precipitate can be discarded, but the clear supernatant must be transferred to a small porcelain crucible. Add a drop of 6 M HCl solution to the crucible and slowly evaporate the contents of the crucible to dryness. Hold the crucible using crucible tongs and heat the dry residue using a gas flame until red heat and until no more white fumes are released (ammonium salts). Let the crucible cool. To the residue in the crucible add 2 drops of distilled water and mix. Draw the resulting solution into a dropper and observe whether it is clear. If the solution is clear, place a small drop of the solution on a glass slide. But, if the solution is cloudy, first transfer it to a conical test tube and centrifuge; only then place the clear supernatant on a glass slide. Apply a drop of 10 % $Na_3[Co(NO_2)_6]$ solution to the slide. In the presence of

potassium ions yellow precipitate forms:



pC = 4.

2. Place 3 drops of test solution in a porcelain crucible and evaporate. Moisten a nichrome wire with 37 % HCl solution and using the moist wire bring the dry residue into the colourless part of gas flame. In the presence of potassium compounds, the flame colours violet. If potassium is present and the flame is observed through cobalt glass (to prevent the interference of sodium and calcium ions), the flame looks raspberry red. The flame colours if the amount of potassium is no less than 10^{-6} g.

Copper, lead, arsenic, antimony, and bismuth compounds also colour the flame. Viewed through cobalt glass the flame looks blue or bluish violet; therefore, the presence of these ions makes the detection of potassium difficult.

2. ANALYSIS OF ANIONS

This section describes the detection methods of 18 frequently occurring anions: CO_3^{2-} , MnO_4^- , CrO_4^{2-} , S^{2-} , SO_3^{2-} , SiO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{C}_2\text{O}_4^{2-}$, F^- , SO_4^{2-} , PO_4^{3-} , SCN^- , I^- , Br^- , Cl^- , NO_2^- , NO_3^- , and BO_2^- .

It is advisable to try to detect these anions in the order in which they are listed. This sequence is established based on practical considerations; one must first examine whether anions present interfere with detection of other ions and then separate the interfering anions.

Methods described here are applicable if only the above-mentioned anions are present in the mixture. If the solution contains other anions than the listed, the methods described here may give erroneous results. Also, the solution may contain only Na^+ , K^+ , and NH_4^+ cations. Other cations must be separated prior analysis as shown on page 63, Chapter 5.

To test the presence of all 18 anions by the methods specified here, 5...6 cm^3 of the test solution are required. It is desirable that the concentration of each ion in the solution is 0.1...0.5 mol/dm^3 .

Before the detection of specific anions, it is advisable to conduct some preliminary tests. Based on the results of the preliminary tests, it is often possible to significantly shorten the course of further analysis.

Preliminary tests must also be done carefully. It can even be recommended to repeat them. For example, if by negligence the presence of a reducing anion is not detected and in the course of analysis it is not attempted to detect these anions, the results will be incorrect. It is also recommended to evaluate the results of preliminary tests after the presence of all ions is already tested. For example, if the solution does not contain thiosulfate ions and if silver nitrate in the presence of nitric acid is added to solution and white precipitate forms, and in the course of analysis neither chloride nor thiocyanate ions have been found, then this indicates that the tests were inaccurate and must be repeated.

2.1. Preliminary tests

1. Detection of oxidizing anions.

- Place a drop of 3 M H_2SO_4 solution in a cavity of a drop plate, add a drop of 1 % KI solution and then the test solution. If MnO_4^- , CrO_4^{2-} or NO_2^- ions are present, they oxidize the iodide ions to free iodine, so the colour of the solution is yellow, orange or reddish brown.
- Place 3 drops of 1 % solution of diphenylamine in concentrated sulfuric acid in a cavity of a drop plate, then add a drop of the test solution. If the test solution contains MnO_4^- , CrO_4^{2-} , NO_2^- or NO_3^- ions, diphenylamine is oxidized. Diphenylamine oxidation products are dark blue, so the reaction is very sensitive. If these oxidants are present in significant quantities, the colour is so dark that the mixture looks like blue ink.

If the test a. gives a negative result, but the test b. — a positive result, it may be indirectly concluded that the solution contains nitrate ions.

2. Detection of reducing anions.

- Place a drop of 3 M H_2SO_4 solution in a cavity of a drop plate, add a drop of 0.002 M (~0.03 %) KMnO_4 solution and a few drops of the test solution. Mix. If there are S^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, SCN^- , I^- , Br^- or NO_2^- ions present, the permanganate ions are reduced and the violet colour disappears. Permanganate ions are also reduced (in 2...15 min) by $\text{C}_2\text{O}_4^{2-}$ and Cl^- .
- If the attempt a. gives a positive result, then using a dropper place a small drop of the test solution on a zinc nitroprusside paper. In the presence of sulfide ions the spot on the reagent paper is violet, but in the presence of sulfite ions the spot is reddish brown (see page 34, Section 2.5.).

3. Precipitation of silver salts. This test must only be done, if the solution does not contain sulfide ions (see 2 b. test). Place a drop of the test solution in a conical test tube, add a drop of 6 M HNO_3 . If precipitation (cloudiness) does not appear in less than 5 min, add several drops of 0.1 M AgNO_3 solution to the acidified test solution. In the presence of Cl^- or SCN^- ions white precipitate forms, but in the presence of I^- or Br^-

ions yellow precipitate forms.

If during the acidification of the test solution with nitric acid it becomes cloudy, heat the test tube in a water bath for 10 min and then centrifuge. Add silver nitrate as described above to the clear supernatant.

4. pH test. Using a dropper or a glass rod place a small drop of the test solution on a universal pH indicator paper. Compare the resulting colour to the colour scale.

If pH is not greater than 8, there cannot be considerable quantities of CO_3^{2-} , S^{2-} , and SiO_3^{2-} ions present in the test solution.

2.2. Detection of CO_3^{2-}

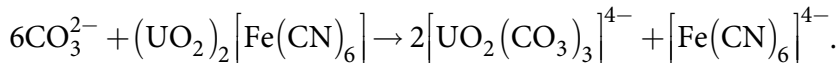
1. Place 5 drops of 6 M CH_3COOH solution in a conical test tube and warm it in a water bath. Rapidly add several drops of test solution to the hot acetic acid. If the test solution contains carbonate ions, gas bubbles are released:



pC = 2.5.

Weak evolution of gas is also observed in the presence of NO_2^- , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, and S^{2-} ions if the concentration of these ions is high. Small amounts of carbonate ions cannot be detected in such case.

2. Place a drop of the test solution in a cavity of a drop plate, add 3 drops of uranyl hexacyanoferrate(II) solution. The disappearance of the maroon colour of the reagent shows the presence of carbonate ions:



The reaction is quite sensitive (pC = 4). Unfortunately, a similar effect is also produced by F^- or BO_2^- ions.

3. Place 15...20 drops of the test solution in a porcelain crucible, add 5 drops of 10 % H_2O_2 solution, and carefully evaporate the mixture to an almost dry state. Cool. Dilute the residue with 3 drops of distilled water; transfer the mixture into a conical test tube and add 3 drops of 6 M HCl. In the presence of carbonate ions effervescence appears (see test 1).

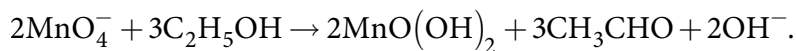
2.3. Detection of MnO_4^-

Noticeable amounts of permanganate ions can only be found in the solution if has pink or violet colour.

$$pC = 6.$$

However, the presence of permanganate ions cannot be conclusively proven only by the colour of the solution, as other compounds (mainly organic substances) may also give a similar hue.

To make sure that the colour of the solution is directly due to permanganate ions, place 2 drops of the coloured test solution in a conical test tube, add a drop of ethanol and heat it in a water bath. In the presence of permanganate ions, the violet (pink) colour of the solution disappears and brown precipitate forms.



Note. If besides permanganate ions chromate ions are also present in the test solution (in this case the solution tends to be reddish), then the solution does not become colourless but acquires a yellow tinge after heating it in the presence of ethanol.

It is recommended that the brown precipitate is centrifuged, washed, and dissolved in a mixture of 2 drops of 6 M HNO_3 and 1 drop of 10% H_2O_2 . Heat the solution until no gas bubbles are released, and then add a small amount of NaBiO_3 . If the solution is red or violet, this unambiguously indicates that the test solution contains permanganate ions.

If permanganate ions are found in the test solution, they must be separated because they hinder the detection of many other ions. Place 3...4 cm^3 of the test solution in a conical test tube, add 3 drops of ethanol and heat the test tube in a water bath until the violet colour disappears (if necessary, add a few more drops of ethanol and continue to heat). Separate $\text{MnO}(\text{OH})_2$ precipitate by centrifugation. Use the resulting clear supernatant to detect the rest of the anions.

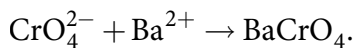
At the same time it must be taken into account that, if the test solution (even if it is alkaline) contains permanganate ions, it cannot contain S^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, SCN^- , and I^- ions.

2.4. Detection of CrO_4^{2-}

1. **Chromate (or dichromate ions)** may be present in the test solution in significant quantities only if its colour is yellow or orange.

pC = 4.7.

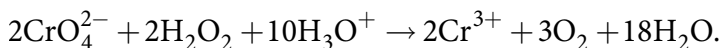
2. Place 2...3 drops of the test solution in a conical test tube, add a few drops of acetate buffer (pH ~ 4) and a few drops of 10 % BaCl_2 solution. In the presence of chromate ions yellow precipitate forms:



pC = 5.

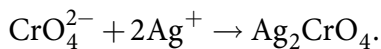
Presence of reducing agents interferes with the test; when the test solution is acidified they reduce chromate ions to Cr(III) ions.

3. Place a drop of the test solution in a conical test tube, add 5...6 drops of saturated complexone III solution and a drop of 10 % H_2O_2 solution. Heat the test tube in a water bath. If the solution contains chromate ions, they are reduced to Cr(III) ions, which subsequently form a violet chromium(III) complexonate (see page 20, Section 1.13):



pC = 3.7.

4. Place a drop of neutral or slightly alkaline test solution in a conical test tube, add 0.1 M AgNO_3 solution. In the presence of chromate ions reddish brown precipitate forms:

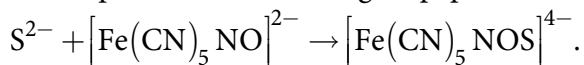


pC = 4.5.

Many other anions under the same conditions form poorly soluble silver salts; besides that these salts may be formed before the silver chromate. Therefore, always add silver nitrate solution in excess.

2.5. Detection of S^{2-}

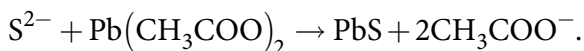
1. Using a capillary dropper place a small drop of neutral or weakly alkaline test solution on a zinc nitroprusside paper. In the presence of sulfide ions a violet spot forms on the reagent paper:



pC = 3.5.

Sulfite ions give a reddish brown spot on a zinc nitroprusside paper, so they more or less hinder the detection of sulfide ions.

2. Using a capillary dropper place a small drop of the test solution on a lead acetate paper. In the presence of sulfide ions a black or gray spot forms on the reagent paper:



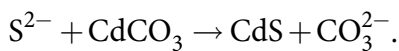
pC = 5.3.

3. Using a capillary dropper place a small drop of neutral or weakly alkaline test solution on a malachite green paper. In the presence of sulfide ions the wetted place on the paper loses colour.

pC = 3.8.

Sulfite ions also decolour malachite green.

4. Place a drop of the test solution in a cavity of a drop plate, add a small amount of $CdCO_3$, and mix with a glass rod. In the presence of sulfide ions the mixture turns yellow:

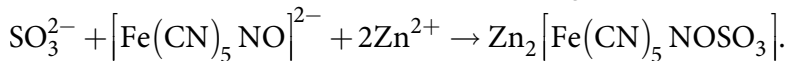


pC = 4.

Sulfide ions interfere with detection of several anions, so the last reaction is also used for the separation of sulfide ions from the test of the solution. For this purpose, pour 2...3 cm³ of the test solution containing sulfide ions into a conical test tube, add ~0.2 g $CdCO_3$, and every few minutes mix with a glass rod. After 15 min centrifuge the mixture. Add a little $CdCO_3$ to the clear supernatant. If practically all sulfide ions have already precipitated from the solution, the mixture will not become yellow. Otherwise, continue processing with $CdCO_3$.

2.6. Detection of SO_3^{2-}

1. Using a capillary dropper place a small drop of neutral or weakly alkaline test solution on a zinc nitroprusside paper. In the presence of sulfite ions a reddish brown spot forms on the reagent paper:

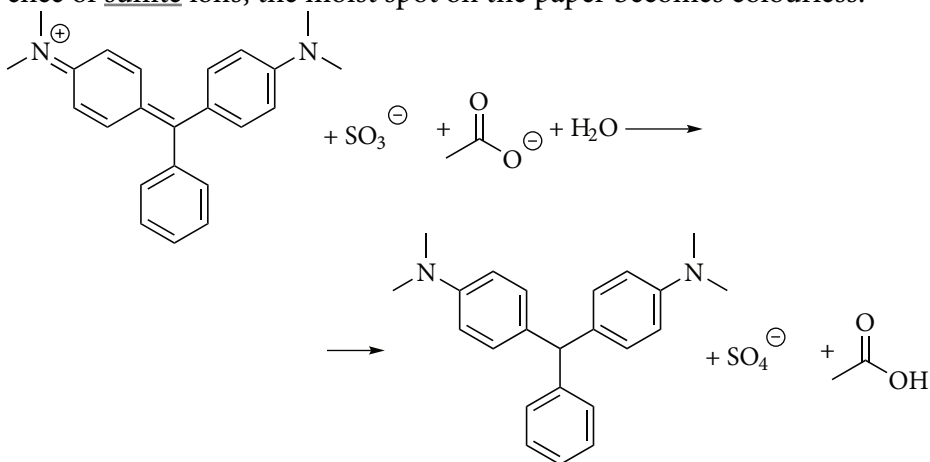


pC = 3.6.

If small quantities of sulfide ions are present in the solution besides sulfite ions, the resulting spot has a violet centre, but the border is reddish brown. Larger quantities of sulfide ions must be previously separated using CdCO_3 as shown on page 34, Section 2.5.

Sulfide ions result in bluish violet spots that usually disappear within a few minutes, and the place retains a pale brownish hue; this does not indicate the presence of sulfite ions. Therefore, we can conclude that small quantities of sulfite ions cannot be detected in the presence of sulfide ions.

2. Place a drop of the test solution in a cavity of a drop plate and mix it with a drop of 1 M $\text{CH}_3\text{COONH}_4$ solution. Using a capillary dropper place a small drop of the mixture on a malachite green paper. In the presence of sulfite ions, the moist spot on the paper becomes colourless.

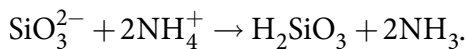


pC = 3.3.

Sulfide ions produce a similar reaction.

2.7. Detection of SiO_3^{2-}

Place 10 drops of the test solution that does not contain sulfide ions (see page 34, Section 2.5 for their detection and separation) in a conical test tube, add 10...15 drops of 1 M $(\text{NH}_4)_2\text{CO}_3$ solution and heat in a water bath. In the presence of silicate ions gel-like or flaky silicic acid precipitate forms:



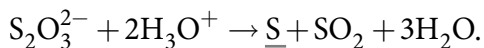
pC = 2.6.

Note. If the test solution does not contain thiosulfate ions, ammonium carbonate can be replaced by ammonium chloride or ammonium nitrate.

Retain the supernatant for detection of $\text{S}_2\text{O}_3^{2-}$, PO_4^{3-} , and $\text{C}_2\text{O}_4^{2-}$ ions.

2.8. Detection of $\text{S}_2\text{O}_3^{2-}$

Make sure that the test solution does not contain S^{2-} and SiO_3^{2-} ions (the detection and separation of these ions is shown in Section 2.5 and in Section 2.7). Place 5 drops of the test solution in a conical test tube and while stirring with a glass rod add 6 M HCl until $\text{pH} \leq 1$. Heat the test tube in a water bath. In the presence of thiosulfate ions, the acidified solution becomes cloudy and shows opalescence after a few seconds or minutes (depending on the ion concentration):



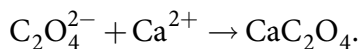
pC = 3.3.

If the solution has become cloudy, continue to heat the test tube in a water bath for another ~10 min to fully decompose the dissolved thiosulfate ions. Centrifuge. Discard the precipitate but retain the supernatant for detection of oxalate ions.

2.9. Detection of $\text{C}_2\text{O}_4^{2-}$

Make sure that the test solution does not contain S^{2-} , SiO_3^{2-} , and $\text{S}_2\text{O}_3^{2-}$ ions (it is recommended to use the supernatant, obtained after the test for the presence of $\text{S}_2\text{O}_3^{2-}$, for this purpose; see Section 2.8). Place

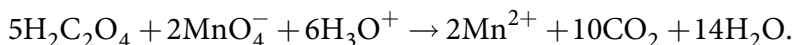
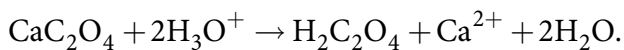
5 drops of the test solution in a conical test tube, add 6 M CH_3COOH drop by drop while stirring until pH 4 (!) is reached, then add 20...25 drops of clear, saturated CaSO_4 solution (the so-called gypsum water). If oxalate ions are present, white crystalline precipitate forms:



pC = 3.5.

In the presence of fluoride ions under these conditions amorphous CaF_2 precipitate forms.

To ensure that the precipitate contains CaC_2O_4 , centrifuge. Discard the supernatant. Wash the precipitate three times thoroughly with 1 cm^3 portions of distilled water. To the washed precipitate add 2 drops of 3 M H_2SO_4 , a drop of 0.01 M MnSO_4 solution, a drop of 0.3% KMnO_4 solution and mix. In the presence of oxalate ions the reddish violet colour disappears because oxalic acid present in the solution reduces permanganate ions. The added manganese(II) ions catalytically accelerate the reduction:



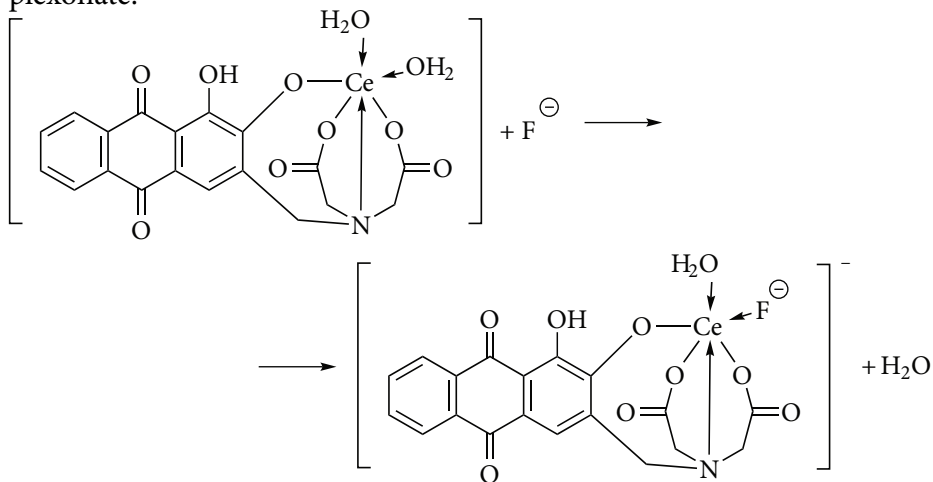
2.10. Detection of F^-

1. Place a drop of the test solution in a 15 cm^3 test tube, dilute with distilled water to 15 cm^3 , and mix.

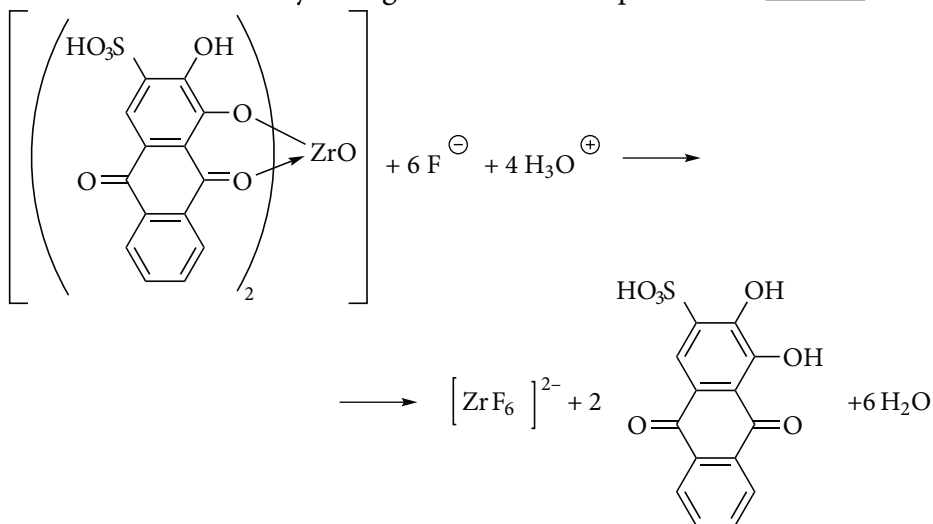
Note. The strong dilution of the test solution prevents the interference of other anions but does not interfere with the detection of fluoride ions because of the high sensitivity of the reaction.

Place one drop of the diluted test solution in a cavity of a drop plate, but in the adjacent cavity place a drop of distilled water. In both cavities add a drop of 0.001 M alizarin complexone solution in acetate buffer system (pH 4.3) and a drop of 0.001 M cerium(III) salt solution. Mix. In the cavity with the test solution within a few minutes a yellow colour appears in the presence of fluoride ions; this contrasts well with the bluish-violet colour in the next cavity, where fluoride ions are not present.

Fluoride ions form a mixed complex with cerium(III)-alizarin-complexonate:



2. Place a drop of the test solution in a cavity of a drop plate, add a drop of 6 M CH_3COOH , swirl the drop plate (!), add a drop of zirconyl alizarin reagent, and mix. If the violet colour of the reagent becomes yellow, add one more drop of the reagent and mix again. Repeated yellowing of the solution is a fairly strong indication of the presence of fluoride ions:



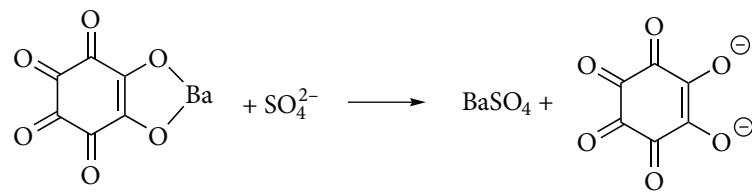
pC = 3.5.

If borate ions are also present in the solution, fluoride ions are bound in the relatively stable $[\text{BF}_4]^-$ ion, and the violet colour switches to yellow only after 5...10 min.

Oxalate ions and to a lesser extent also phosphate ions give the same effect as fluoride ions, so it is better to use the reaction with cerium(III)-alizarin-complexonate than the reaction with zirconyl alizarin.

2.11. Detection of SO_4^{2-}

1. Place a drop of the test solution in a cavity of a drop plate, add a drop of 1 M $\text{CH}_3\text{COONH}_4$ solution. Using a capillary dropper place a small amount of the resulting mixture on a barium rhodizonate paper. In the presence of sulfate ions, a yellow spot appears on the reagent paper within a few seconds:

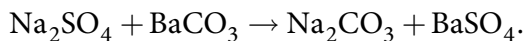


pC = 3.5.

Oxalate ions react similarly to sulfate ions. If the yellow spot does not appear, it is clear that no sulfate ions are present in the test solution or that the concentration of sulfate ions is less than 0.003 mol/dm^3 .

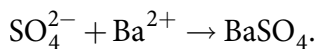
2. Place 5 drops of the test solution in a small porcelain crucible and while stirring with a glass rod add 6 M HCl until the solution is acidic. Then evaporate the solution to dryness. Dissolve the dry residue in 3 drops of water, add about 30 mg of BaCO_3 , and a drop of 1 % thymolphthalein solution in 50 % ethanol. Mix.

If the test solution contains alkali sulfates, Na_2CO_3 forms in the reaction with BaCO_3 ; the resulting Na_2CO_3 colours thymolphthalein blue, for example:



3. Place 3 drops of the test solution that does not contain sulfide ions

(see page 34, Section 2.5) in a conical test tube. Add 25 drops of distilled water, 3 drops of 6 M HCl, and 3 drops of 10 % BaCl₂ solution. In the presence of sulfate ions white crystalline precipitate immediately appears:

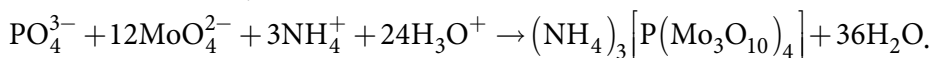


Thiosulfate ions that emit sulfur in an acidic environment interfere with detection of sulfate ions. However, if BaCl₂ solution is added immediately after acidification and precipitate immediately forms, one can be sure to that sulfate ions are present.

In the described conditions sulfur usually forms from thiosulfate ions only after ~1 min, counting from the moment of the acidification of the solution.

2.12. Detection of PO₄³⁻

1. Place 3 drops of the test solution in a conical test tube, add 2 drops of 65 % HNO₃ solution, and heat for 10 min in a water bath to oxidize any reducing agents that are present. Cool the solution and add 20...30 drops of molybdate reagent. In the presence of phosphate ions the solution becomes yellow, and gradually bright yellow precipitate of ammonium phosphomolybdate forms:

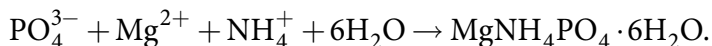


If NH₄NO₃ is added the yellow precipitate forms more rapidly.

pC = 4.5.

Arsenate ions give a similar reaction if the solution is heated.

2. Place 3 drops of the test solution that does not contain silicate ions (see the demonstration and separation on page 36, Section 2.7) in a conical test tube. While stirring with a glass rod, slowly add 15 drops of the so-called mixture of magnesium (magnesium nitrate solution in ammonium buffer). In the presence of phosphate ions, white crystalline precipitate forms:



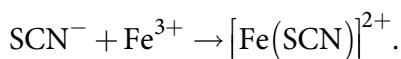
pC = 3.

To make sure that the precipitate is crystalline, place some precipitate on a glass slide and observe under a microscope. $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ crystals look like snowflakes.

In the presence of CO_3^{2-} , SiO_3^{2-} , and F^- ions, amorphous precipitate may form.

2.13. Detection of SCN^-

Place a drop of the test solution in a conical test tube, add 2 drops of 3 M H_2SO_4 and 3 drops of FeCl_3 solution. In the presence of thiocyanate ions the solution becomes dark red:



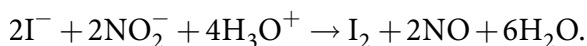
pC = 5.

If strong reducing agents (S^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, I^-) or anions ligands (PO_4^{3-} , $\text{C}_2\text{O}_4^{2-}$, F^-) are present in the test solution, FeCl_3 solution has to be added in greater quantities, but usually no more than 6 drops are needed.

As iodide ions are oxidized by FeCl_3 , iodine forms; iodine colours the solution brownish red. This colour is sometimes mistaken for the colour of iron(III) thiocyanate complex. To avoid this mistake, add 2 cm³ of CCl_4 to the coloured solution and shake vigorously for about 2 min. Iodine is extracted into carbon tetrachloride layer. If the top water layer retains the dark red colour, thiocyanate ions are considered to be detected.

2.14. Detection of I^-

1. Place a drop of the test solution in a conical test tube, add a drop of 6 M CH_3COOH solution and a drop of 1 M KNO_2 solution. In the presence of iodide ions the solution turns yellow, reddish or reddish brown (depending on the ion concentration in the solution):



If 20 drops of CCl_4 are added to the coloured solution and it is shaken vigorously, iodine is extracted into the organic solvent layer; the organic

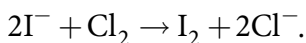
solvent layer is coloured pink or violet.

pC = 5.3.

If in the solution also contains SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, and S^{2-} , several drops of KNO_2 solution must be added.

In the presence of thiocyanate ions the reaction sensitivity significantly decreases.

2. Place 3 drops of the test solution in a test tube, add 20 drops of distilled water, a drop of 3 M H_2SO_4 , 20 drops of CCl_4 , and shaking the test tube vigorously add chlorine water drop by drop. If the test solution contains iodide ions, they are oxidized to iodine that is extracted into carbon tetrachloride layer and colours the layer pink or violet:



pC = 5.

If reducing agents that are more powerful than iodide ions (such as S^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$) are also present in the solution, these anions are oxidized first with chlorine water; only after this free iodine forms. In such cases add more chlorine water drop by drop. It must be taken into account that excess of chlorine water is not desirable. Needlessly added excess chlorine oxidizes the resulting iodine to colourless iodic acid:



If the violet (pink) colour fades or does not appear at all, the presence of iodide ions can go unnoticed.

If the test solution contains oxidising anions (CrO_4^{2-} , NO_2^-), the formation of iodine is often observed as the solution is acidified, before chlorine water is even added.

Note. The described test generally proceeds well if chlorine water is fresh and a strong chlorine smell is felt. It is better to replace weak chlorine water with sodium or potassium nitrite solution. Only in this case it is better to acidify the test solution with acetic acid.

2.15. Detection of Br⁻

1. Place a drop of the test solution in a conical test tube, add 5 drops of saturated KMnO₄ solution, and heat for 3 min in a water bath to oxidize the dissolved reducing agents. If during heating the violet colour of the solution disappears, add a little more KMnO₄ and additionally heat the solution for at least 3 min. Then add 5 drops of 6 M CH₃COOH, 5 drops of saturated CuSO₄ solution and close the test tube with a stopper (with a glass pipe in the middle of the stopper). Place a fluorescein paper into the glass pipe, as shown in Fig. 9. Continue to heat the test tube for 5 min in a water bath.

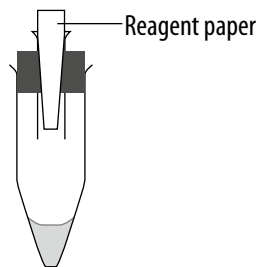
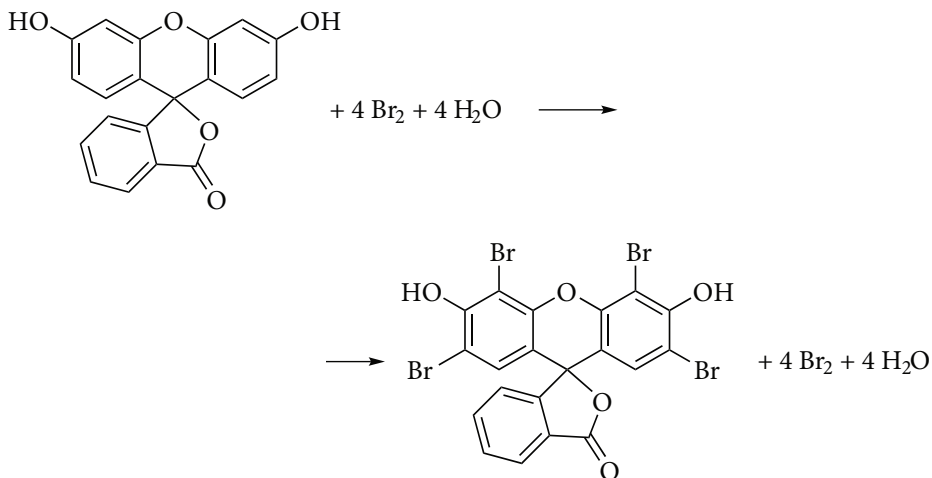


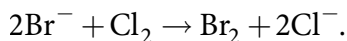
Fig. 9. Apparatus for identification of volatile reaction products.

Bromide ions present in the test solution form bromine, which reacts with fluorescein to form tetrabromofluorescein (eosin). As a result the yellow fluorescein paper partially or completely turns pink:



Large quantities of thiocyanate ions interfere with the detection of bromide ions.

2. Place 5 drops of the test solution in the test tube, add 3 drops of 3 M H_2SO_4 and 20...30 drops of CCl_4 , and while shaking the test tube vigorously add chlorine water drop by drop. If bromide ions are present in the solution, they are oxidised to bromine and extracted into the carbon tetrachloride layer. Bromine colours the layer yellow, orange or reddish brown, depending on the amount of bromine released:



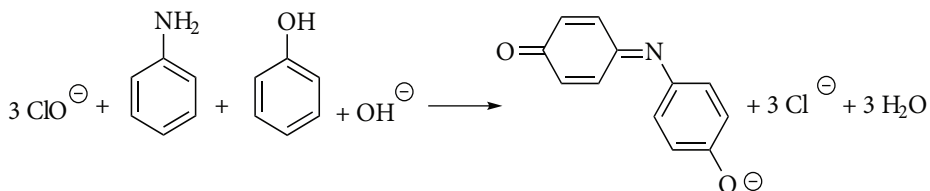
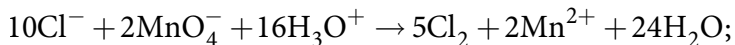
pC = 4.3.

If the test solution also contains iodide ions, the carbon tetrachloride layer first colours pink or violet. In this case, continue to add chlorine water while vigorously shaking the solution until pink (violet) colour disappears, as iodine is oxidised to iodic acid (see detection of iodide ions). If the pink colour turns orange, then it shows that the test solution contained both iodide ions and bromide ions at the same time.

In case the test solution contains large amounts of more powerful reducing agents or chlorine water is of low concentration, add chlorine water in large quantities. If a lot of chlorine water has been added, but the orange colour does not appear, it can be tentatively concluded that there are no bromide ions in the solution. But, before such conclusion is reached, it is recommended to add one drop of 1 M KBr solution to the solution and shake vigorously. If the carbon tetrachloride layer colours orange, then one can be sure that there were no bromide ions in the initial test solution. But, if after adding bromide ions there is still no colour, then this indicates that chlorine water has been added in excess. In this situation the test has to be repeated. In the repeated test one of the following must be done: a smaller amount of the test solution has to be analysed, fresh chlorine water has to be prepared or, simply, the existing chlorine water has to be added in even larger quantities.

2.16. Detection of Cl⁻

Place a drop of the test solution in a conical test tube, add 10 drops of saturated KMnO₄ solution, and heat in a water bath. If during heating the violet colour of the solution disappears, add a few more drops of KMnO₄ solution. After 5 min add 3 drops of 6 M CH₃COOH solution, continue to heat for a few minutes to completely oxidize other reducing agents present and to volatilize any bromine that may have formed from bromide ions. Also, be sure that the colour of the solution at all times is violet. Make sure that all bromine has been released using fluorescein paper, as shown in Fig. 9. Then add 3 drops of 96% H₂SO₄ to the solution, replace the fluorescein paper with a filter paper strip moistened with Deniz reagent and continue heating in a water bath. In presence of sulfuric acid chloride ions are oxidised to chlorine. Chlorine ends up on the filter paper where hypochlorite ions form. They in turn oxidize the components of Deniz reagent — aniline and phenol to indophenolate ions that are blue:

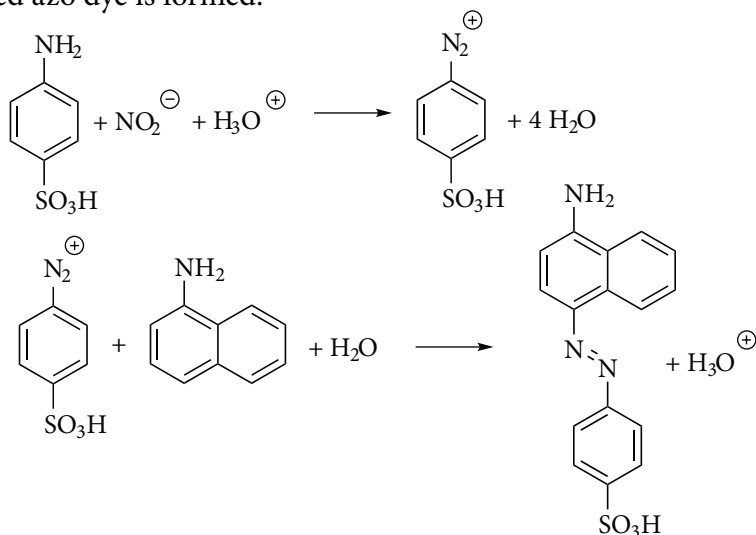


In the presence of chloride ions the ongoing reactions on the filter paper strip moistened with Deniz reagent turn it blue. But, if the chloride ion concentration is high, the lower end of the paper strip may even appear brownish.

If the reagent is sufficiently fresh and the test is executed correctly, then a pale bluish colouration indicates that chloride ions are present only in small amounts. At noteworthy concentrations of chloride ions, a brownish tone appears.

2.17. Detection of NO_2^-

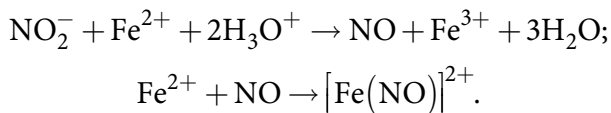
1. Place a drop of the test solution in a test tube, add 5 cm^3 of distilled water and 5 drops of Griess-Ilosvay's reagent. In the presence of nitrite ions red azo dye is formed:



pC = 6.7.

If the nitrite ion concentration in the solution is high, then after a short time the solution turns brownish or brown as the formed azo dyes precipitate.

2. Place a drop of 3 M H_2SO_4 in a conical test tube, add a few $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystals. Mix. In the presence of nitrite ions the solution becomes greenish-brown:



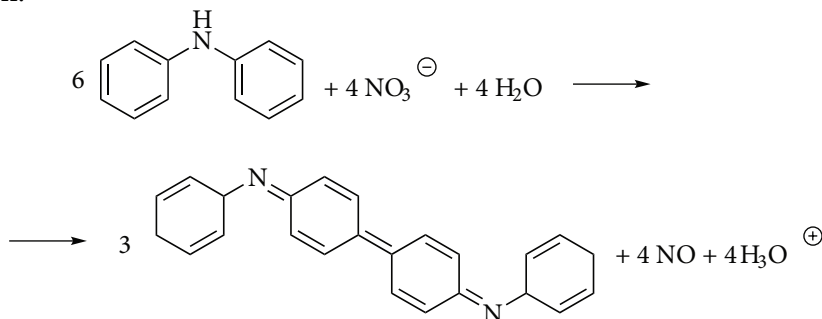
pC = 3.7.

In the presence of SCN^- red $[\text{Fe}(\text{SCN})]^{2+}$ forms, so the colour of $[\text{Fe}(\text{NO})]^{2+}$ is not visible. In the presence of S^{2-} black FeS precipitate forms, but the precipitate disappears and does not interfere with the detection of NO_2^- if the solution is mixed.

2.18. Detection of NO_3^-

○ If the solution does not contain NO_2^- .

1. Place a drop of the test solution in a cavity of a drop plate, add 4...5 mg of anhydrous Na_2SO_3 , and a drop of 96 % H_2SO_4 . Mix with a glass rod. To the resulting mixture add 5 drops of 1 % diphenylamine in 96 % sulfuric acid solution and mix again with the same glass rod. In the presence of nitrate ions dark blue diphenylamine oxidation products form:

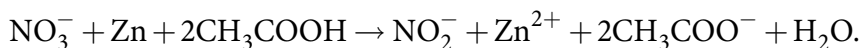


pC = 5.

Note. In the presence of a significant amount of nitrate ions, the intensity of the blue colour resembles blue ink. If the colour is lighter, nitrate ions in the test solution are present only as small impurities.

Note. Taking into account the high sensitivity of the reaction, very carefully wash the drop plate and the glass rod before starting the test. It is also recommended to do a control test in the adjacent cavity of the drop plate using a drop of distilled water in place of the test solution. In this way one can make sure that the auxiliary agents used (H_2SO_4 , Na_2SO_3) are pure enough.

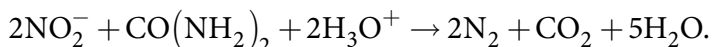
2. Place a drop of the test solution in a cavity of a drop plate, add a drop of 6 M CH_3COOH solution, a drop of Griess-Ilosvay's reagent, and a Zn pellet. In presence of acetic acid the nitrate ions are reduced to nitrite ions:



Resulting nitrite ions react with Griess-Ilosvay's reagent and form red azo dye (see page 46, Section 2.17). Therefore, a violet-red border forms around the zinc granule after a few minutes. If nitrate ion concentration in the test solution is high, brown precipitate gradually forms around the granule.

○ If the solution contains NO_2^- .

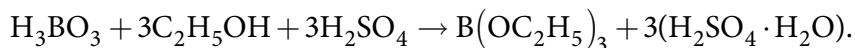
Place a drop of the test solution in a test tube, add a drop of 30 % urea solution, and shake. Then add 1 M H_2SO_4 solution drop by drop until the test solution becomes acidic. Nitrite ions are reduced to free nitrogen:



After 5 min place a drop of the resulting solution into another test tube, add 1 cm^3 of distilled water and two drops of Griess-Ilosvay's reagent. If within a few minutes the solution does not become pink, then nitrite ions are reduced practically completely. In this case add about 10 cm^3 of distilled water to the remainder of the solution in the 10...15 cm^3 test tube and mix. Place a drop of the diluted solution in a cavity of a drop plate, add 5 drops of 1 % diphenylamine solution in 96 % sulfuric acid, and stir with a clean glass rod. If the test solution contains nitrate ions in considerable quantities, it at once colours dark-blue (see page 47).

2.19. Detection of BO_2^-

Place 10 drops of test solution in a porcelain crucible and evaporate to dryness. Let the crucible cool. Add 6 drops of 96 % H_2SO_4 and 1 cm^3 of ethanol to the dry residue, mix with a glass rod. Volatile boric acid triethyl ester is formed:



Ignite the mixture in a dark area. In the presence of boron compounds the flame is greenish.

pC = 3.

If the test solution contains MnO_4^- or CrO_4^{2-} , then add several drops of 3 M H_2SO_4 and 0.1 g of Na_2SO_3 prior to evaporation.

3. MICROANALYSIS

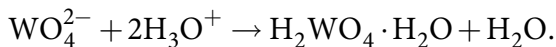
IN THE PRESENCE OF SOME RARE ELEMENTS

Modern materials used today may contain an extensive range of elements. The determination of individual components in such objects is sometimes quite difficult because highly selective analytical methods are still relatively few in number.

A simplified example of such analysis methods is described here — a microanalysis method for detection of 12 different ions in a mixture. Among these ions, five are the ions of the so-called rare elements: WO_4^{2-} , MoO_4^{2-} , VO_3^- , Ti(IV), and Zr(IV). The analysis takes about 30 min, and about 0.1 cm^3 (3 drops) of the test solution are used.

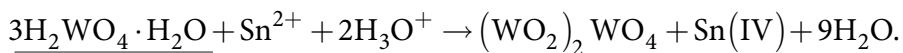
3.1. Detection of WO_4^{2-}

Place a drop of the test solution (or suspension, if the solution is cloudy) in a conical test tube, add a drop of 1 M ZnSO_4 solution in 4 M hydrochloric acid, and heat for 5 min in a water bath. In the presence of tungstate ions, the solution becomes (remains) cloudy because tungstic acid is formed, and it is poorly soluble:



Centrifuge. Transfer the clear solution (supernatant) into another conical test tube and use it for the next test.

After separation of the supernatant, wash the precipitate with 1 cm^3 of 0.6 M HCl. Discard the washing solution. Add 5 drops of 37% HCl solution to the precipitate, then add a few bright $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ crystals, mix with a glass rod, and heat in a water bath. If the sediment contains tungstic acid, the mixture turns blue:

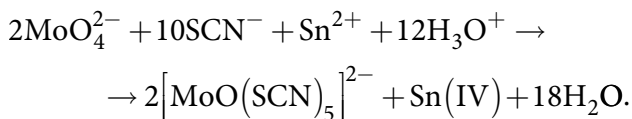


3.2. Detection of MoO_4^{2-} , VO_3^- , Ti(IV) , Zr(IV) , Cu^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , and Ni^{2+}

Place a small amount of the clear solution (supernatant) obtained in the first test on the following reagent papers using a capillary dropper:

- on a **thiocyanate** (rhodanide) paper a reddish brown spot immediately appears if iron(III) ions are present in the solution (see page 12, Section 1.6). If the resulting reddish brown spot is moistened with 2 M HCl solution saturated with SnCl_2 , the colour of iron(III) thiocyanate complex disappears within a few seconds.

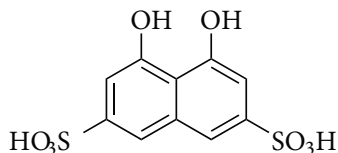
If placing a small amount of the solution on a thiocyanate paper first results in a yellow spot which then gradually turns orange and red, it indicates the presence of molybdate ion. If the spot is moistened with the SnCl_2 solution as mentioned above, the intensity of red colour should increase or the reddish brown colour should shift to red violet:



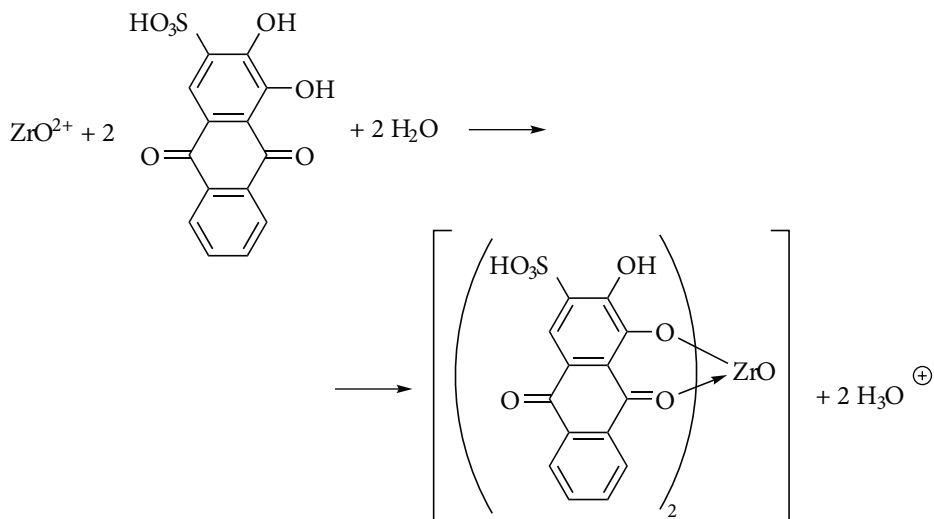
If the reddish brown spot that immediately forms on the thiocyanate paper does not disappear after wetting it with SnCl_2 solution (often it may acquire a violet hue), then this indicates that Fe^{3+} and MoO_4^{2-} are present in the solution simultaneously;

- on a **o-phenanthroline** paper an orange red spot or ring gradually forms in presence of iron(II) ions (see page 12, Section 1.6);
- on a **diacetyldioxime** paper a pink spot or ring gradually forms in presence of nickel ions (see page 13, Section 1.6);
- on a **chromotropic acid** paper a brown or reddish brown spot (that often becomes violet brown upon desiccation) forms in presence of titanium(IV) ions. Titanium(IV) ions form a complex of an unknown composition with chromotropic acid.

The formula of chromotropic acid:



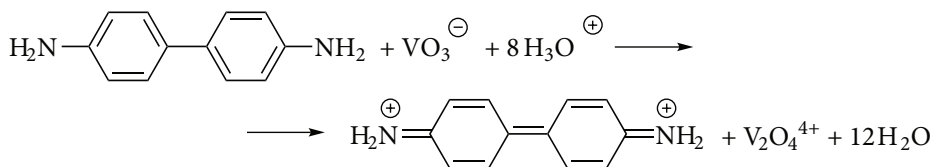
- on a **sulfoalizarine** paper a violet or pink spot forms in presence of **zirconium** ions:



Yellow sulfoalizarine paper often becomes reddish or violet by itself during storage, but such paper is still usable. If the acidified test solution is placed on such paper, the reagent paper recovers the original bright yellow colour. In presence of zirconium ions the middle part of the wet spot is pink or violet and has a yellow border.

Molybdate ions on a sulfoalizarine paper give an orange or pink spot; therefore, they interfere with detection of zirconium ions. The colour generated by molybdate ions disappears if the coloured spot is additionally moistened with 3 M HCl. Unfortunately these conditions also reduce the stability of zirconium complex, and therefore it is practically impossible to detect low quantities of zirconium ions in the presence of molybdate ions using a sulfoalizarine paper;

- on a **benzidine** paper a yellow spot forms in presence of vanadate ions:



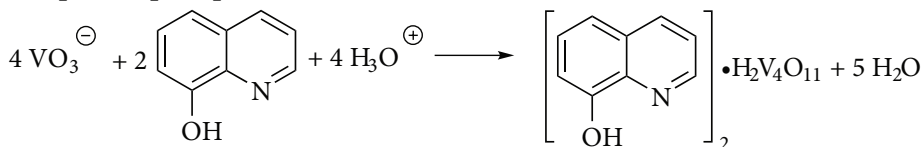
The yellow spot turns blue if it is moistened with a solution of $\text{CH}_3\text{COONH}_4$;

- on a **tetrarhodanomercurate (tetrathiocyanatomercurate)** paper a bright blue spot forms in presence of cobalt ions — $(\text{Zn},\text{Co})[\text{Hg}(\text{SCN})_4]$; a dirty violet spot forms in the presence of copper ions — $(\text{Zn},\text{Cu})[\text{Hg}(\text{SCN})_4]$. A dirty blue spot (sometimes the centre of the spot is violet, but the borders are blue) forms if the solution contains both cobalt and copper ions in approximately equal quantities.

Presence of iron(II) ions and large quantities of iron(III) ions interfere with the detection; to prevent this interference see page 13, Section 1.6.

3.3. Detection of VO_3^-

After the second test add a drop of 6 M $\text{CH}_3\text{COONH}_4$ solution to the remaining supernatant obtained after separation of tungstic acid. Then add 2 drops of 3 % 8-hydroxyquinoline acidified with acetic acid and heat for 5 min in a boiling water bath. In presence of vanadate ions a yellow compound precipitates:



The compound turns into a blue-black compound of unknown composition when heated. The blue-black compound can be extracted using butanol; the butanol layer colours brownish or reddish brown.

3.4. Detection of Mn^{2+}

Place a drop of the test solution in a cavity of a drop plate, add a drop of 6 M HNO_3 solution and ~20 mg of NaBiO_3 . Stir with a glass rod. If the solution contains manganese(II) ions, they are oxidized to permanganate ions, so a pink (violet) colour appears (see page 20, Section 1.12).

3.5. Detection of Cr^{3+}

Place a drop of the test solution in a conical test tube, add 2 drops of 6 M NaOH solution, 2 drops of 10 % H_2O_2 solution, and heat for 5 min in a water bath. Centrifuge. In the presence of chromium ions the clear supernatant is yellow or yellow-green (see page 20, Section 1.13).

4. WASTE WATER ANALYSIS

Complex of measures for nature protection includes the care for purity of natural waters to protect them from contamination by untreated waste water of various origins.

The following text describes methods of analysis of natural waters. The detection of 12 more or less undesirable ions is described: Fe^{3+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Hg^{2+} , Cu^{2+} , As(III, V) , SO_4^{2-} , NO_2^- , I^- , SCN^- , PO_4^{3-} . The analysis requires about 200 cm^3 of the waste water.

4.1. Detection of Fe^{3+} , Co^{2+} , Ni^{2+} , and Mn^{2+}

Pour 100 cm^3 of the waste water into a $200\text{--}300 \text{ cm}^3$ beaker, add 1 cm^3 1 M MgCl_2 solution, and while stirring with a glass rod add 37 % HCl solution until the test solution reaches pH 1. Heat the acidified solution to boiling point and while stirring add 10 % NaOH solution until stable precipitate that does not disappear upon stirring forms. Then add another 5 cm^3 of 10 % NaOH solution in excess. Any dissolved iron(III), cobalt, nickel, and manganese ions are co-precipitated with magnesium hydroxide, for example:



Allow the solution to cool and the insoluble precipitate to settle. During this time one can carry out the rest of the tests (2–9).

After an hour carefully decant most of the clear supernatant from the precipitate. Agitate the sediment in the remaining supernatant, transfer the suspension into two conical test tubes, and centrifuge them for 5 min, so the sediment layer becomes as dense as possible. After centrifugation discard the clear supernatant and wash the precipitate with 2 cm^3 of distilled water.

Retain one of the conical test tubes with the precipitate to repeat the test if it becomes necessary. But dissolve the precipitate in the second test tube by adding 3...4 drops of 6 M HNO_3 while heating in a water bath. If insoluble brown flakes — $\text{MnO}(\text{OH})_2$ — remain

in the test tube, add a drop of 10% H_2O_2 solution and continue to heat for another 10 min in a water bath.

Add a drop of 1 M ZnSO_4 solution to the resulting solution. Using a capillary dropper transfer a part of the solution acidified by nitric acid on these reagent papers:

- on a **rhodanide (thiocyanate)** paper a reddish brown spot appears in presence of iron(III) ions (see page 12, Section 1.6);
- on a **tetrarhodanomercurate (tetrathiocyanatomercurate)** paper a bluish spot appears after a few minutes in presence of cobalt ions (see page 13, Section 1.6).

If the solution contains both cobalt ions and copper ions, which both co-precipitated with magnesium hydroxide, a dirty blue spot appears on the tetrarhodanomercurate paper. If the solution does not contain cobalt ions but it does contain copper ions, a dirty violet spot appears on the reagent paper;

- on a **diacetyldioxime** paper a pink spot or ring gradually forms in presence of nickel ions (see page 13, Section 1.6).

If cobalt or copper ions are present in the solution together with nickel ions, the spot is brownish pink.

To the remainder of the solution acidified nitric acid in the conical test tube, add another 2...3 drops of 6 M HNO_3 solution, 1 cm^3 of distilled water, 30...50 mg NaBiO_3 and mix with a glass rod. In the presence of manganese ions the solution gradually colours pink or violet because permanganate ions are formed (see page 20, Section 1.12).

If the concentration manganese ions is very low, the pink colour of the solution is easier to see after centrifugation.

4.2. Detection of As(III, V)

Pour 25 cm^3 of the waste water into 50 cm^3 bottle of a Zangger-Black's apparatus (see Fig. 1), add 5 cm^3 of 9 M H_2SO_4 solution, some $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ crystals, and 2.5 g Zn (5 granules). Immediately close the bottle by covering it with the stopper. The corrugated lead acetate paper must be inserted into thickest lower pipe, but the mercury(II) bromide or chloride

paper must be inserted into the thin top pipe. If the waste water contains arsenic compounds, mercury halide paper colours yellow, orange or brown (see page 10, Section 1.4). The colouration can be obtained faster or slower, depending on the concentration of arsenic compounds and other ions. If no interfering ions are present, then the time it takes for the reagent paper to colour, the height of the colour band, and the shade of the colour roughly indicates the arsenic concentration in the waste water (Table 1).

Table 1.
Detection of arsenic in the waste water using a HgBr_2 paper

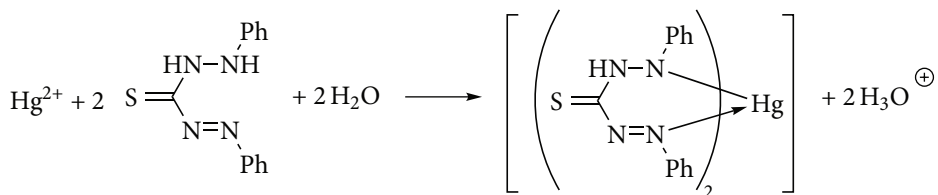
| | C, mg/dm^3 | | Hue and height of the coloured band (mm) on a HgBr_2 paper | | |
|---|----------------------------|----|---|------------------|---------------------|
| | As | Hg | 20 min | 40 min | 60 min |
| 1 | 0.03 | – | – | – | pale yellow (0.5) |
| 2 | 0.10 | – | – | very pale yellow | yellow (1.0) |
| 3 | 0.30 | – | – | yellow | yellow (2.5) |
| 4 | 1.00 | – | pale yellow | yellow | orange-yellow (7.5) |
| 5 | 3.00 | – | yellow | orange-yellow | brownish (9.0) |
| 6 | 1.00 | 10 | – | – | pale yellow (1.0) |
| 7 | 1.00 | 40 | – | – | – |
| 8 | 3.00 | 40 | – | – | yellow (1.0) |
| 9 | 10.00 | 40 | pale yellow | orange-yellow | orange-yellow (4.0) |

See page 10, Section 1.4 about the impact of presence of other ions on the test. The effect of mercury ions on the test is presented in Table 1. For example, if concentration of arsenic ions in the solution is $1 \text{ mg}/\text{dm}^3$ and no interfering ions are present, then the presence of arsenic can be detected as early as after 20 min, but within an hour orange-yellow band 7.5 mm in height forms on the HgBr_2 paper. In the presence of $10 \text{ mg}/\text{dm}^3$ Hg, the same concentration of arsenic can be detected only after an hour, but if the mercury ion concentration reaches $40 \text{ mg}/\text{dm}^3$, then no colouration on the reagent paper occurs even after an hour.

Note. In waste water samples that are issued to students, arsenic concentration is generally no less than $15 \text{ mg}/\text{dm}^3$ and the concentration of mercury ions does not exceed $40 \text{ mg}/\text{dm}^3$. Thus, in these samples the presence of arsenic can be detected relatively well.

4.3. Detection of Hg²⁺

Pour 5 cm³ of the waste water into a 10...15 cm³ test tube, add 1 cm³ of acetate buffer (pH 4), 6 drops of saturated solution of complexone III, and 1 cm³ of 0.01 % dithizone solution in carbon tetrachloride. Close the test tube with a polyethylene or glass stopper and shake vigorously. The green colour of the reagent in the presence of mercury(II) ions will become yellow or orange:



4.4. Detection of Cu²⁺

Pour 5 cm³ of the waste water into a 10...15 cm³ test tube, add 2 drops of 6 M HCl solution, 2 drops of 10 % KI solution, and 0.5 cm³ of lead diethyldithiocarbamate solution in carbon tetrachloride. Close the test tube with a polyethylene or glass stopper and shake vigorously for about 2 min. Allow the liquid layers to separate. Depending on copper ion concentration, yellow or brownish colour appears in the lower layer that consists of carbon tetrachloride (see Table 2):

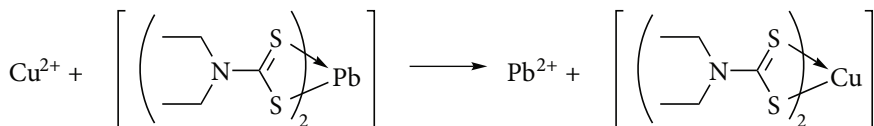


Table 2.
Detection of copper ions using lead diethyldithiocarbamate

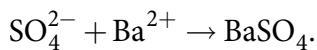
| Copper ion concentration, mg/dm ³ | Carbon tetrachloride layer colour |
|--|-----------------------------------|
| 80 | light brown |
| 50 | pale brown |
| 10 | yellow brown |
| 5 | brownish yellow |
| 1 | bright yellow |
| 0.5 | yellow |
| 0.1 | pale yellow |
| 0.05 | very pale yellow |

Nitrite ions and other oxidizing agents, if any are present, interfere with copper ions, as they oxidize the added iodide ions to the free iodine and, thus, colour the carbon tetrachloride layer pink or violet. The yellow or brownish colour of diethyldithiocarbamate complex is difficult to see under these conditions.

Interference of nitrite ions can be prevented. For this purpose, when the waste water sample is acidified with hydrochloric acid and KI solution is added, also add 4...5 drops of saturated carbamide solution and gently heat the test tube for 10 min in a gas flame until the yellow colour of solution disappears or becomes pale. Cool the test tube and only then add lead diethyldithiocarbamate solution and shake as described above.

4.5. Detection of SO₄²⁻

Pour 5 cm³ of the waste water into a 10...15 cm³ test tube, add 3 drops of 37 % HCl solution and 10 drops of 10 % BaCl₂ solution. In the presence of sulfate ions the solution immediately or after a few minutes becomes turbid:



If there is doubt about the occurrence of turbidity, it is recommended to pour 5 cm³ of the waste water into a second test tube of the same size

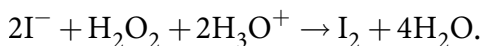
and to add 3 drops of 37 % HCl, but not to add BaCl₂ solution. If the contents of the first test tube are even slightly more turbid than the contents of the second test tube, then the waste water sample contains sulfate ions (it is better to examine the test tubes using a dark background).

4.6. Detection of NO₂⁻

Pour 5 cm³ of the waste water into a 10...15 cm³ test tube, add 3 drops of 37 % HCl and 10 drops of Griess-Ilosvay's reagent. In the presence of nitrite ions the test solution becomes very pink in a few minutes (see page 46). Pale pink colour sometimes is caused by the reagent itself as nitrogen oxides may be present in the laboratory air. Nitrogen oxides are soluble in water and form nitrite ions.

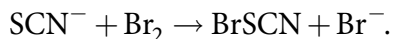
4.7. Detection of I⁻

Pour 5 cm³ of the waste water into a 10...15 cm³ test tube, add 10 drops of 6 M CH₃COOH solution, 3 drops of 10 % H₂O₂ solution, and 1 cm³ of CCl₄. Close the test tube with a polyethylene or glass stopper and shake vigorously. If iodide ions are present in the waste water sample, they are oxidized to free iodine and extracted into carbon tetrachloride colouring it pink or violet:



4.8. Detection of SCN⁻

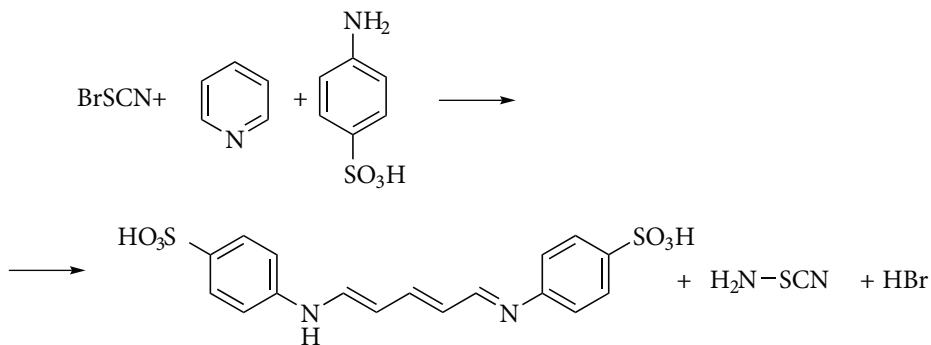
Place 2 cm³ of neutral or slightly acidic waste water into a 10...15 cm³ test tube, add 5 drops of bromine water, and mix. If thiocyanate ions are present in the waste water, bromo thiocyanate forms:



The excess of bromine can be bound by adding 0.5 % solution of hydrazine sulfate until the yellow colour of the solution disappears and then adding one more drop.

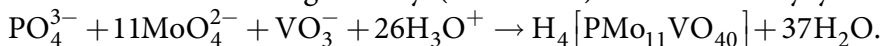
Place 3 cm³ pyridine reagent and 0.5 cm³ of 1 % sulfanilic acid solution in a second test tube with the same size and mix. Then mix the

contents of the two test tubes by pouring the mixture from one test tube to another. In the presence of thiocyanate ion the solution colours orange or yellow:



4.9. Detection of PO_4^{3-}

Place 5 cm³ of the waste water into a 10...15 cm³ test tube, add 1 cm³ of vanadate-molybdate reagent. In the presence of phosphate ions the solution gradually (5...10 min) turns intensely yellow:



It is preferable to carry out an „empty” test with 5 cm³ of distilled water in parallel. The colour intensities of both solutions should differ significantly.

5. GENERAL INSTRUCTIONS FOR ANALYSIS OF OBJECTS

Due to the small number of hours devoted to object analysis within the curriculum, test specimens given to students have a quite simple composition — mainly oxide, hydroxide or salt mixtures, fertilizers, metal alloys etc.

All cations and anions (the total number of which does not exceed 6) present in the test object are those detection of which is described in 1st to 3rd chapters of this teaching aid. The following will not be given as test objects: silicates insoluble in acids, difficult to dissolve metal alloys, and complex compounds which require special techniques for degradation.

The received test object must be first observed visually. Typically, it is quite easy to tell from the appearance of the object whether it is metallic (metal alloy) or non-metallic.

Metals and their alloys can be quite easily distinguished. For example, aluminium and magnesium alloys are lightweight, and aluminium alloys are soluble in alkaline solutions. Alloys that contain a lot of iron, cobalt or nickel are attracted to magnets. Copper alloys (but not all!) are characterized by yellow or reddish colour. After these tests it is preferable to try to dissolve the alloy in 6 M HNO₃ solution. Iron alloys dissolve easily, and the solution turns yellowish brown; in the presence of thiocyanate ions the solution colours crimson — [Fe(SCN)]²⁺. Most copper alloys also dissolve in nitric acid. Then the solution obtains a bluish colour if diluted with water, but in the presence of ammonia it colours dark blue due to formation of [Cu(NH₃)₄]²⁺. If the alloy contains tin or antimony (bronzes, metals for printing, Babbitts, solders etc.), during the dissolution white precipitate forms (H₂SnO₃, HSbO₃). Aluminium and chrome alloys are practically insoluble in nitric acid (due to passivation). Aluminium alloys are usually first dissolved in an alkaline solution: aluminium dissolves, but other alloying metals remain as solids. It is easier to dissolve chromium alloys in aqua regia.

If an alloy is dissolved in acid, the excess of the acid should be removed

by evaporating the resulting solution to a small volume (~3 drops). Dilute the evaporated solution with 2 cm³ of water and use it to detect specific metal ions in the alloy. In order to identify precipitated stannic acid and antimononic acid that have formed by dissolving the alloy in nitric acid, it is preferable to dissolve them in 37 % hydrochloric acid. Use one part of the solution to demonstrate the presence of tin by flame reaction (page 11, Section 1.5), and use the second part of the solution to detect antimony using Zangger-Black's apparatus (page 10, Section 1.4).

In these metal alloys alkali and alkaline earth ions are not to be detected.

If the test object is non-metallic, it is advised first to pay attention to its colour (use chemist manuals for more information!). Then check the solubility of the test object in water (also while heating). If the test object dissolves in water, it may contain sodium, potassium, and ammonium salts of any anions, or in the presence of other cations it may contain only a very limited number of anions (mostly nitrates, chlorides, sulfates). In this case it is also recommended to use solubility tables. If the test object does not dissolve completely in water, make sure that a part of it is dissolved. For this purpose centrifuge the turbid solution, place a drop of the clear supernatant on a glass slide, and evaporate to dryness. If considerable remnants of salts are left on the glass slide, it indicates that a part of the object has dissolved. It is recommended to analyze the supernatant (that is, the aqueous solution) separately.

If the sample does not dissolve in water partially or fully, treat it with 6 M HCl solution. Most of the salts of weak acids as well as many oxides and hydroxides dissolve under these conditions. It is compulsory to pay attention to the dissolving process because gases may be released as the test object reacts with the acid (CO₂ — from carbonates, SO₂ — from sulfites and thiosulfates, H₂S — from some sulfides). It should be noted that nitrites are relatively soluble in water, so their presence here is not expected.

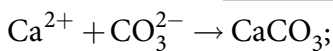
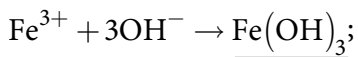
If the test object does not dissolve in hydrochloric acid, it is recommended to treat it with 67 % HNO₃ solution or even with aqua regia while

heating. These acids dissolve some very poorly soluble sulfides — HgS, CuS, PbS etc. Sulfide ions in these compounds are oxidized to sulfur or sulfate ions.

If the test object (or a part of it) is not dissolved in nitric acid or aqua regia, then this so-called **insoluble** residue may contain BaSO₄, SrSO₄, (CaSO₄), PbSO₄, AgCl, AgBr, AgI, calcined oxides — Al₂O₃, Cr₂O₃, Fe₂O₃, SnO₂, Sb₂O₃, and a few others. These compounds must be converted into soluble compounds as shown in the literature [1, 2, 4, 5, 12]. In these sources valuable guidance on analysis of various objects is also given.

Test objects dissolved in water and acids can be analyzed as shown in the 1st and 2nd chapters of this teaching aid. The specified methods can be used without modification only in the absence of interfering ions. However, most cations interfere with the detection of anions, while the presence of many anions complicates the detection of cations. Therefore, the interfering ions are usually separated before the detection of cations and anions.

One of the easiest ways to separate most of the cations from anions is the so-called preparation of **carbonate decoction**. For this purpose place the solution to be analyzed or the dry substance in a test tube, add 1 M Na₂CO₃ solution (sometimes also dry Na₂CO₃) until the mixture gives strongly alkaline reaction, and heat it for ~15 min in a water bath, stirring occasionally. Under these conditions most of the cations form poorly soluble hydroxides, carbonates or basic carbonates, such as:



Pour the resulting mixture into conical test tubes and centrifuge. Retain the precipitate. Transfer the supernatant to another test tube and stir while gently adding acetic acid solution drop by drop until the pH reaches 8. If during the neutralization of the solution further precipitation occurs (for example, aluminium hydroxide from the aluminates formed during

the preparation of carbonate decoction, basic copper or nickel carbonates from the respective ammonium complexes etc.), centrifuge again. Use the neutralized clear supernatant to detect anions.

It is recommended to combine the precipitate that has formed during preparation of carbonate decoction and during the neutralization of supernatant. Dissolve the combined precipitate by heating it with the minimum amount of 6 M nitric acid. Use the resulting solution to detect cations.

References

1. Алексеев В.Н. Курс качественного химического полумикроанализа. – 5-е изд., перераб. и доп. – М.: Химия, 1973. – 584 с.
2. Алимарин И.П., Архангельская В.Н. Качественный полумикроанализ. – М.-Л.: Госхимиздат, 1952. – 260 с.
3. Бабко А.К., Пилипенко А.Т. Фотометрический анализ: Методы определения неметаллов. – М.: Химия, 1974. – 360 с.
4. Клячко Ю.А., Шапиро С.А. Курс химического качественного анализа. – М.: Госхимиздат, 1960. – 702 с.
5. Крешков А.П. Основы аналитической химии. Ч.1. Теоретические основы. Качественный анализ. – 4-е изд., перераб. – М.: Химия, 1976. – 472 с.
6. Лабораторные работы по качественному анализу./ Сост. Я.К.Путнинь. - Рига: Риж.политехн.ин-т, 1979. – 26 с.
7. Лабораторные работы по качественному анализу. Ч.2./ Сост. Я.К.Путнинь. - Рига: Риж.политехн.ин-т, 1981. – 35 с.
8. Лурье Ю.Ю., Рыбникова А.И. Химический анализ производственных сточных вод. – М.: Химия, 1974. – 336 с.
9. Мурашова В.И., Тананаева А.Н., Ховякова Р.Ф. Качественный химический дробный анализ. – М.: Химия, 1976. – 280 с.
10. Набиванец В.И. Дробные методы анализа: Учебное пособие. – Киев: Киевский политехн.ин-т, 1979. – 44 с.
11. Путнинь Я.К. Применение реактивных бумаг в качественном химическом анализе. – Рига: Риж.политехн.ин-т, 1973. – 32 с.
12. Путнинь Я.К., Янсон Э.Ю. Практикум по качественному анализу. – Рига: Риж.политехн.ин-т, 1975. – 102 с.
13. Реакции и реактивы для качественного анализа неорганических соединений / Под ред. А.С.Комаровского.- М.-Л.: Госхимиздат, 1950. - 248 с.
14. Тананаев Н.А. Дробный анализ. – М.-Л.: Госхимиздат, 1950. – 248 с.
15. Тананаев Н.А. Капельный метод. – М.-Л.: Госхимиздат, 1954. – 272 с.

16. Унифицированные методы анализа вод / Под ред. Ю.Ю.Лурье. – 2-е изд.,испр. – М.: Химия, 1973. – 376 с.
17. Файгль Ф., Ангер В. Капельный анализ неорганических веществ. – М.: Мир, 1976. Т.1. 392 с. Т.2. 320 с.
18. Окач А. Qualitative analytische Chemie. – Leipzig: AVG, 1960. – 644 S.
19. Chang R. Chemistry. – 6th ed. – Boston: McGraw-Hill, 1998. – 995 p.
20. Laboratory Experiments for Chemistry. The Central Science. – Thirteenth Edition / J. H. Nelson, M. Stoltzfus, K. C. Kemp and M. Lufaso. – Pearson Education, 2016. – 673 p.

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