IDENTIFICATION OF CHEMICAL AND PHASE COMPOSITION

(learning support)

The pedagogical text

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Ostrava 2013
Name: Identification of chemical and phase composition
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Edition: first, 2013
Number of pages: 47

Studying materials for Thermal Engineering and Ceramic Materials at the Faculty of Metallurgy and Material Engineering.

Linguistic proofreading: has not been performed.

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1. Introduction

Time for study 60 minutes

Goal After studying this section you will be able to

- define the basic methods of identification
- list the methods of chemical analysis
- list the methods of phase analysis

Lecture

The content here will be a summary of identification methods and the characterization of materials industry, i.e., glass, ceramic products and their semi products, their hydration and furthermore, of different raw materials (natural and secondary, i.e. industrial waste).

The basic methods:

A. The methods of chemical, classical and spectral (instrumental) analysis.

B. The methods of phase analysis (microscopy, x-ray phase analysis, x-ray microanalysis, the methods of thermal analysis, chemical extraction).

C. The assessment methods for the textures and microstructures (microscopy, electron microscopy, porosimetry, the determination of specific surfaces).

D. The assessment of material reactivity as commercial properties - mainly cements and latently hydraulic substances (calorimetry, enthalpiometry).

E. Other methods (pH, conductivity, etc.).

For each assessment a representative sample shall be used. The procedures for obtaining (sampling) an average sample are given in the standards. The principle: by quartering the reduction up to a multiple quantity needed for one determination. Samples with a wide interval of abrasiveness in the appropriate quantity are ground and then further quartered (not in monitoring the texture, etc.).

We work mostly with dry samples, either in their natural state, or are appropriately finished dry.
The choice of procedure:

1. According to the quantity of a sample.
2. According to the request for speed setting.
3. In accordance with the procedure laid down in a relevant standard.

Chemically we determine either elements (exceptionally) or oxides (except for non-oxide ceramics, there shall be elements determined). After the chemical composition is known, this is plotted on a ternary graph and we can use it to identify the phase composition (of minerals).

Methods may be:

- qualitative - the findings of components (we will learn what elements, oxides, phases are there, but not their quantity)
- quantitative - the findings of contents (learning about the quantity)

A. THE METHODS OF CHEMICAL ANALYSIS

These are the qualitative and quantitative methods.

1. Gravimetric method - we separate a constituent from the other parts and weight it.
2. Volumetric analysis (titration) - finding the volume of reagent that we must add to the quantitative execution of a reaction with a determined component (using indicators).
3. Spectral (optical) analysis - the sample shall be monitored on the basis of the interaction with a visible light illumination. It is divided into emission and absorption.
4. X-ray fluorescence analysis - the use of x-ray radiation and its interaction with matter. This method will help to find elements.
5. X-ray microanalysis - the volume of x-ray beams directed to e.g. a defect in a material.
6. Enthalpimetry - a method that determines chemical components in a supply solution on the basis of heat developing when a reagent is added.

B. THE METHODS OF ANALYSIS PHASE

These are the qualitative methods.

1. Optical microscopy
2. X-ray diffraction analysis - x-rays are released on the sample and then we let the trainees perform diffraction. This is the most accessible method.
3. Infrared spectroscopy.
4. Thermal analysis - simultaneously a sample is heated and some of its macroscopic properties are measured.
5. Calorimetry.

### A summary of the chapter

- The basic methods for identification.
- Chemical and phase analysis.

### Questions for the subject studied

1. Explain the concepts of quantity and quality.
2. List the methods of chemical analysis.
3. List the methods of phase analysis.
2. The methods of chemical analysis

**Time for study** 180 minutes

**Goal** After studying this paragraph you will be able to
- define the basic analytic operations

**Lecture**

Basic analytic operations - weighing, the preparing of solutions, dissolving, melting, coagulation, filtering, drying, annealing, titration, etc.

Volumetric and other glass - beakers, funnels, cups, graduated cylinders, burets and pipettes (calibrated to spill), pycnometers, volumetric flasks (calibrated for pouring).

When taking the sample from the supplier for chemical analysis we must take into account the quantity of the supplied sample, and the due time of this analysis. The procedure for sample acceptance:

a) According to the standards.

b) Agree on a procedure (e.g. with a customer).

c) Be aware who does what work and how much does it cost.

The preparation of volumetric solutions - analytical reagents shall be prepared with the exact concentration, for washing, pH adjustments, buffers, etc. solutions with the approximate concentration are prepared.

**Placing the sample into the solution**

Approximately correct - means to weigh approximately 1 g, but to be correct up to four decimal places.

First we need to prepare a representative proportion of the sample.

1. From the coach, using the required methods, we take approximately a 30 kg sample.

2. We dry the sample for the constant weight.

3. A sample is ground to a suitable granularity.

4. Quartering - we heap the sample up, flatten it with a plate to a cake, and quarter it up to the quantity of a few grams.
5. From the obtained quantities we now directly weigh a sample for our analysis and create a reserve solution.

a) Direct dissolution in the acids (mostly HCl).

b) The insoluble in HCl (mostly a mixture of HF + H₂SO₄).

c) Melting.

ad 5a) direct dissolution in the acids

The dissolution of samples in the acids, mostly in HCl, to obtain the solution of chlorides. The insoluble remains SiO₂, which gives the gel SiO₂·nH₂O (H₂SiO₃).

- carbonates: CaCO₃ + 2HCl → CaCl₂ + H₂SiO₃ + 2H₂O.

- some oxides: MgO + 2HCl → MgCl₂ + H₂O.

- clinker minerals:
  3CaO·SiO₂ + 6HCl → 3CaCl₂ + H₂SiO₃ + 6H₂O,
  3CaO·Al₂O₃ + 12HCl → 3CaCl₂ + 2AlCl₃ + 6H₂O,
  4CaO·Al₂O₃·Fe₂O₃ + 20HCl → 4CaCl₂ + 2AlCl₃ + 2FeCl₃ + 10H₂O.

- hydroxides: Ca(OH)₂ + 2HCl → CaCl₂ + 2H₂O.

The dissolution is connected with a double evaporation to dryness, so that the gel H₂SiO₃ is well-packed up and then filtered (otherwise colloidal H₂SiO₃ transfers to the reserve solution, and obstructs when establishing other components). With evaporation the rest of HCl is removed, emerged chlorides are well soluble in water.

Transfer of cement into the solution - weigh the sample of cement exactly, and transfer it quantitatively to a beaker. Add the amount of HCl recommended by the standard and place the flask in a water bath. Boil until the sample is dried (the HCl reacts to chlorides and SiO₂ is precipitated in the form of H₂SiO₃). Pour the hot distilled water, all chlorides are dissolved and go into the solution, and only the insoluble gel H₂SiO₃ remains, which is later filtered. This means that the lower bowl remains with a clear solution of chlorides, and on a filter paper the gel H₂SiO₃ will remain. Following the subsequent drying and tempering of this gel we will get the amount of SiO₂ in the original sample of cement.

ad 5b) insoluble in HCl

When analysing the glass, glass sands, quartz, etc. the decomposition of mixtures HF + H₂SO₄ is used: HF decomposes all silicates with the emergence of SiF₄. H₂SO₄ removes emerging water (SiO₂ + 4HF → SiF₄ + 2H₂O) and thus shifts the balance of the response to the right.

Concentrated H₂SO₄ has oxidizing properties, therefore it dissolves even noble metals and their alloys. Apart from that to certain metals and ores some mixtures of acids are used: nitrohydrochloric acid (1 part of HCl + 3 parts HNO₃, oxidation here supplies emerging chlorine), or even reversed nitrohydrochloric acid (the opposite ratio).

ad 5c) melting
Products insoluble in the acids are e.g. by melting converted to a form soluble in HCl (acids). They are melted in furnaces or over a flare, they melt in the autoclave or a microwave (while hot).

- Alkaline-carbonate melting: as flux is used the anhydrous Na$_2$CO$_3$ (melting point of 849 °C), K$_2$CO$_3$ (melting point of 909 °C) or their mixture of 1:1. The sample is mixed with an excess of carbonate, it is melted in a Petri dish until a clear melt is reached. There arise alkaline silicates and aluminates which are subsequently soluble in diluted HCl (except for SiO$_2$, which again gives an insoluble gel SiO$_2$.nH$_2$O). Examples: kaolinite Al$_2$O$_3$.2SiO$_2$.2H$_2$O + 3Na$_2$CO$_3$ → 2Na$_2$SiO$_3$ + 2NaAlO$_2$ + 2H$_2$O + 3CO$_2$

felspar K$_2$O.Al$_2$O$_3$.6SiO$_2$ + 7Na$_2$CO$_3$ → K$_2$CO$_3$ + 6Na$_2$SiO$_3$ + 2NaAlO$_2$ + 6CO$_2$.

Similarly clays, feldspars, slags, ashes, etc. are melted.

- Alkaline melting: the mixture Na$_2$CO$_3$ + Na$_2$B$_4$O$_7$.10H$_2$O (1:1), after dissolution in HCl there must be multiple evaporation with HCl, using methanol to remove H$_3$BO$_3$.

- Alkaline oxidation melting: in the mixture Na$_2$CO$_3$ + NaNO$_3$. This way the chromium ores, ferrosilicon, ceramic and refractory materials are melted. An oxidizer is mixed in a ratio 1/10. Similarly, you can use the mixture of Na$_2$CO$_3$ + Na$_2$O$_2$.

- Melting using KHSO$_4$: this dehydrates when heated with disulfate potassium emerging: 2KHSO$_4$ → K$_2$S$_2$O$_7$ + H$_2$O, z K$_2$S$_2$O$_7$ at higher temperature SO$_3$ releases and this reacts with metals (Al, Fe, Cr, Mo etc.) to soluble sulphates Al$_2$O$_3$ + 3K$_2$S$_2$O$_7$ → Al$_2$(SO$_4$)$_3$ + 3K$_2$SO$_4$. It is used for aluminates, spinels, and some silicates.

- Acid melting with NH$_4$Cl: used on some oxides, e.g. ZrO$_2$.

- Melting with NaOH (melting point of 318 °C) or KOH (melting point of 360 °C) at temperatures of 500 to 600°C in a silver crucible is used e.g. for bauxite, carbides, cherts etc. Problem - alkalis can not be determined here!

A summary of the chapter

- The mass fraction.
- Preparation of a solution with a known concentration.
- Determining the exact concentration.
- Preparation of a molar solution.
- Placing the sample into the solution.
Questions for the subject studied

1. Name analytical operations.
2. Define mass fraction.
3. Define the relations used to prepare a solution by dilution.
4. Define the relations used to prepare a solution of a known concentration.
5. Describe the procedure to place a sample into a solution.
2.1. Gravimetric setting

**Time for study** 90 minutes

**Goal** After studying this paragraph you will be able to

- define the direct and indirect methods of gravimetric determination
- describe the precipitation of solutions

**Lecture**

In principle it is about establishing certain components of the sample weighed with the highest possible precision (analytical scales). We distinguish these procedures:

1. Indirect methods of determination - the content of a constituent is found as the difference of the mass between the input and output sample, from which the ingredient is removed.

   a) Loss on drying - sample (1 to 3 g) is dried at a temperature of 105 to 110 °C (or according to the specified temperature) until reaching a constant weight. The sample is put into a weighting boat \((m_a)\) to dry for 2 hours, then left to cool in a desiccator, and then it is weighed. It is dried further for e.g. 0.5 hours, then it is left to cool, weighed again, etc. until a constant weight is obtained \((m_b)\).

   \[
   \%\text{H}_2\text{O} = \frac{m_a - m_b}{m_a} \cdot 100
   \]

   b) The loss on ignition - a sample is ignited in a porcelain crucible back to a constant weight. The calculation is similar to that used for the loss on drying (starting from a dry sample).

2. Direct determination methods - the content of a determined constituent (mostly oxides) is examined quantitatively after it is isolated (from a certain portion of this sample) in the form of a clean and stable substance with a defined composition, i.e. the precipitates. Chemical reactions leading to precipitate occurrence, which is separated from the solution of other ingredients that are chosen, so that their balance is quantitatively shifted to the right, in order to be prepared quickly enough. The precipitate is separated (filtered), washed, dried or annealed (with this it is obtained in a defined chemical form), weighed, and the representation of a given constituent in the sample is calculated.

   The precipitation means excretion of a little soluble substance by adding an indicator into the solution. It is best when there is a large and well filterable crystals. The emerging precipitate shall have a minimum solubility in the solution, from which it is precipitated. Vice versa in the process of precipitation the precipitates are always polluted by other ingredients present in the sample.
solution (mostly adsorbed on a surface and the phenomena are called occlusions and inclusions =
detention of foreign ions in (v) inter crystalline areas).

The rules for the precipitation:

- A precipitate from the diluted solutions, the precipitant must be added slowly, added
  slowly while stirring. Or eventually a precipitate in the presence of an electrolyte
  (NH₄Cl), which improves the coagulation of the precipitate.
- A precipitate at higher temperatures and then let it stand for some time.
- On the filter wash the precipitate, in order to remove the solution and adsorbed ions.

The precipitated form may not be identical to the weighted (stoichiometric) form - it is usually
obtained by annealing. E.g. Al(OH)₃ precipitates but Al₂O₃ is weighed, and similarly H₂SiO₃ and
SiO₂.

General procedure - the weighed quantity of sample (mₛ) is turned into the solution and a reserve
solution of volume V (ml) is prepared. With the use of a pipette we determine an aliquot proportion of
P (ml) from it. Reaction conditions are adjusted (pH, the buffer, temperature), the precipitating agent
is added into a small excess (according to pH), and a determined constituent is excluded in the form of
a low soluble precipitate. After standing the precipitate is filtered, washed, dried and annealed
(weighted form x). Its mass mₜ is determined.

\[ x = \frac{mₚ \cdot V}{mₛ \cdot P} \cdot 100 \quad (\%) \]

In another form it is counted using the whole mass.

Examples of determination:

a) The determination of SiO₂ and the decomposable share - during dissolution we know the
values of sample (n) in HCl, we precipitate a gel of silicic acid (this has a large surface and is
poorly filterable, therefore it is necessary to precipitate it twice and wash). The reserve
solution must remain clear. When annealing the gel of silicic acid we get some quantity of SiO₂
in this sample (x).

\[ \% \text{SiO}_2 = \frac{x}{n} \cdot 100 \]

After more accurate determination by using different procedures we can "remove" SiO₂ and
only the insoluble share will remain. For example, a weighed product in a platinum crucible is
poured with a few drops of diluted H₂SO₄ (1:4) and 10 ml of concentrated HF is added. It
fumes off till dry: SiO₂ + 4HF → SiF₄ + 2H₂O. SiF₄ evaporates and only the insoluble residue
remains, the difference in weight is then the content of SiO₂. The rest is smelted out, dissolved
in HCl and together with the first filtrate (from filtering SiO₂ + insoluble residue) we will
prepare the reserve solution for all determinations.

b) The determination of the R₂O₃ (seskvioxides) - are a common part of pottery: these are the
AL₂O₃, Fe₂O₃, TiO₂, MnO₂, P₂O₅. The determination is made of an aliquots share of (P) from
the reserve solution \((V)\) after establishing SiO\(_2\). We pipette out around 1/3 of the reserve solution after SiO\(_2\) (oxides R\(_2\)O\(_3\) are there in the form of chlorides). The subsequent precipitation shall be done with hydroxides - into a solution taken in hot NH\(_4\)OH is added (e.g. FeCl\(_3\) + 3NH\(_4\)ON \(\rightarrow\) Fe(OH)\(_3\) + 3NH\(_4\)Cl). To highlight the colour transition we add the methyl red indicator (in an acidic environment it has red colour, in alkaline yellow). A few drops of NH\(_4\)OH are added. Stir with a glass stick and during friction between the sticks and the wall of a beaker the nuclei of hydroxides will emerge. It is followed by filtering and washing the filter with a solution of NH\(_4\)Cl. The precipitate anneal into constant weight \((x)\) and the hydroxides become oxides R\(_2\)O\(_3\).

\[
\% \text{ R}_2\text{O}_3 = \frac{x \cdot V}{n \cdot P} \cdot 100
\]

c) The determination of sulphates - we will use the rest in the beaker after establishing the R\(_2\)O\(_3\) (determination of sulphates must be done in the solution and it shall not contain SiO\(_2\) and R\(_2\)O\(_3\)). The volume of the beaker will be boiled, then acidified with a few drops of HNO\(_3\) and while still hot the methyl red indicator is added (serving to check whether the acid solution is acidified enough). Sulphates are precipitated in the form of BaSO\(_4\) by adding BaCl\(_2\). This process takes a long time, it is necessary to let the beaker stand at least for 24 hours, at least for 3 hours at a temperature of 90°C. Then we filter it and anneal it to reach the constant weight. We weigh the precipitate of BaSO\(_4\), but we reflect it as SO\(_3\) content.

\[
\% \text{ SO}_3 = \frac{m_{\text{BaSO}_4}}{n} \cdot \frac{V}{P} \cdot \frac{M_{\text{SO}_3}}{M_{\text{BaSO}_4}} \cdot 100
\]

A summary of the chapter

- Indirect methods of determination.
- Direct determination methods.
- The precipitation.

Questions for the subject studied

1. Describe indirect methods of determination.
2. Explain the direct methods of determination.
3. Explain the concept of precipitation.
4. Specify examples of the determination by precipitation.
2.2. The methods of titrimetric analysis (titration)

Time for study 180 minutes

Goal  After studying this paragraph you will be able to

- define the concept of neutralising titration
- define the concept of redox reaction
- define the concept of precipitation
- define the term complexometry

Lecture

We determine the quantity of the reagent of a known concentration, needed to ensure that the concrete responses with a given component take place till the end, until the equivalent point is reached. Its reaching is determined using an appropriate indicator (which is in an equivalent point, e.g. changing the colour of the entire solution).

In volumetric analysis protolytic reactions (neutralisation), oxidation-reduction, precipitating and complexing are used. The reactions must take place clearly following a certain chemical formula, quickly, to capture an equivalent point. It is identified visually, photometrically, thermometrically, or eventually using electrical methods (potentiometrically = pH, conductometrically = changes in the conductivity of solutions, etc.). Visual indication is possible without an indicator - the colour in solution changes directly, e.g. in oxidation-reduction phenomena (manganitometry, iodometry), mostly using indicators:

- Acid-base (weak acids, alkalis).
- Redox (oxidation reagent reduces itself, but something else is oxidizing).
- The precipitating (indicator with a reagent is forming a coloured precipitate).
- Metalochrome for chelatometry.

Titration is often marked according to the reagent in the burette (acidimetry = titration acid, alkalimetry = titration principle oxidimetry, chelatometry = complexometry, etc.).

The neutralisation reaction

We titrate using acid or an alkali solution of the opposite character. In the vicinity of an equivalent point its pH is rapidly changing, to which the solution reacts e.g. by a step change in colour.

1. Alkalimetry - acid is in the solution and we add alkalis from the burette.
2. **Acidimetry** - in the solution is the alkalis and we add acid from the burette.

Equivalence is emerging at varying pH (with regard to a stronger partner), are therefore indicators are necessary, as they dissociate at various pH (while they change colours). In majority the indicators are weak acids or weak alkalis.

<table>
<thead>
<tr>
<th>name</th>
<th>The pH zone</th>
<th>change of colour with an increase of pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>thymol blue</td>
<td>1.2 - 2.8</td>
<td>red - yellow</td>
</tr>
<tr>
<td>methyl orange</td>
<td>3.1 - 4.4</td>
<td>red - orange yellow</td>
</tr>
<tr>
<td>methyl red indicator</td>
<td>4.4 - 6.2</td>
<td>red - yellow</td>
</tr>
<tr>
<td>bromothymol blue</td>
<td>6.0 - 7.6</td>
<td>yellow - blue</td>
</tr>
<tr>
<td>phenolphthalein</td>
<td>8.0 - 9.6</td>
<td>colourless - red</td>
</tr>
<tr>
<td>thymoldftalein</td>
<td>9.3 - 10.5</td>
<td>colourless - blue</td>
</tr>
</tbody>
</table>

For titration the so-called basic substances are used, i.e. substances that are always prepared with an exact concentration, or solutions of an approximate concentration, which was particularized using titration to some basic substance. Examples of essential substances in the neutralisation analysis are:

a) Anhydrous Na₂CO₃ (for the specification of hydrochloric acid concentration).

b) Dihydrate of oxalic acid (HCOO)₂.2H₂O.

c) Potassium bicarbonate KHCO₃.

d) Hydageniodate potassium KH(JO₃)₂.

Hydrochloric acid is always checked by Na₂CO₃ or KHCO₃, sodium hydroxide is checked with (HCOO)₂.2H₂O.

**Redox reaction**

No indicator is used because the agent is always coloured. Redox reactions are divided according to the reagent used.

a) Permanganometry - we titrate using KMnO₄ (oxidation reagent), used for the determination of Fe²⁺ (oxidized to Fe³⁺).

b) Bromatometry - oxidation reagent KBrO₄

c) Bichromatometry - oxidation reagent to K₂Cr₂O₇

For example in an acid solution the purple Mn⁷⁺ is reduced to pink Mn²⁺, when the solution of KMnO₄ is added as a titration reagent into a solution containing reducing substance (Fe²⁺, Sn²⁺, Al³⁺, Sb⁵⁺).

**Precipitation**

The titration results in hardly soluble precipitate, the equivalent point is indicated potentiometrically, rather than using the indicators. The well-known method is argentometry, in which that titrate reagent is the solution AgNO₃. With different anions in the solution (Cl⁻, Br⁻, I⁻, CN⁻, SCN⁻) insoluble salts are forming (AgCl, ......AgCN......). A significant method to determine these anions.
Complexometry (chelatometry)

It comes from Prof. Schwarzenbach and this is the most important titration method of all.

Mainly the chelaton II (sodium salt of ethylenediamine tetracetic acid) is used and chelaton III (disodium salt of ethylenediamine tetracetic acid - Na$_2$H$_2$Y.2H$_2$O)

Chelaton III:

![Chemical structure of chelaton III](image)

Replacement of the two Hs with Na

This salt in a dissociating in aqueous solution: Na$_2$H$_2$Y → 2Na$^+$ + H$_2$Y$^{2-}$ and the anion H$_2$Y$^{2-}$ provides permanent chelaton complexes with a range of 2$^+$, 3$^+$, 4$^+$ valent cations. According to the valency of a cation either hydrogen is replaced, or even Na$^+$ in the structure and here therefore complexes are created, which vary in charge and stability in various solutions, according to the pH value of the solution.

H$_2$Y$^{2-}$ + Me$^{2+}$ → 2H$^+$ + MeY$^{2-}$ stable in an alkaline environment

H$_2$Y$^{2-}$ + Me$^{3+}$ → 2H$^+$ + MeY$^-$ stable in a neutral and slightly acidic conditions

H$_2$Y$^{2-}$ + Me$^{4+}$ → 2H$^+$ + MeY stable in strongly acidic conditions

The relevant pH range for the possible selective determination of a specific cation is ensured using buffers (the solution keeps constant pH, e.g. alkalis + salt), or they eventually camouflage using other cations (they are weighed in strong neutral complexes). The most frequently determined ingredients:

- Ca$^{2+}$ - pH > 12, indicator fluoroxon: transition from green to the colour pink,
  
  The indicator murexid: a transition from red to a violet colour.

- Mg$^{2+}$ - pH ~ 10, indicator erriochrome black T: transition from a red to blue colour.

- Al$^{3+}$, Fe$^{3+}$, Th$^{4+}$, Ti$^{4+}$, Zr$^{4+}$.

The indicators that are used in complexometry are called metalochrome indicators. They form coloured complexes with cations of metals (an indicator has a different colour). In a container there is an equivalent part of the reserve solution adjusted to its pH to 10, and a small amount of indicator is added (e.g. erriochrome black), which creates a red coloured complex with the Mg$^{2+}$. Chelaton III (CH-3) is slowly added, which reacts with all Ca$^{2+}$ and then Mg$^{2+}$ (binding them to the hard chelate
complex). The last Mg\(^{2+}\) is in the complex with the indicator, it replaces CH\(^{-}\) and removes Mg\(^{2+}\) from this complex, so the indicator remains in its initial state, i.e. the solution turns blue (Mg\(^{2+}\) complex with erriochrome black is weaker than the Mg\(^{2+}\) complex with chelatony). This applies only to certain pH (in this case for pH = 10). One complication is the content of Fe\(^{3+}\). It is linked with erriochrome black to a solid complex, which is not dissolved using chelatony and thus the eriochrome black should remain in its initial state and does not indicate the transition. Therefore, it must bind the Fe\(^{3+}\) in advance into even stronger complex which it gives using trietanolamine.

Chelatony III is a basic substance, its solutions are accurate.

Indicators for complexometry:

<table>
<thead>
<tr>
<th>name</th>
<th>colour of the complex with an indicator</th>
<th>colour of the indicator</th>
<th>interval of pH</th>
<th>cations determined this way</th>
<th>interfering ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erriochrom black T</td>
<td>red</td>
<td>blue</td>
<td>~ 10</td>
<td>Mg(^{2+}), Ca(^{2+}), Zn(^{2+}), Mn(^{2+})</td>
<td>Fe(^{3+})</td>
</tr>
<tr>
<td>Fluorexon</td>
<td>fluorescing green</td>
<td>pink</td>
<td>&gt; 12</td>
<td>Ca(^{2+}), Si(^{2+}), Ba(^{2+})</td>
<td>Zn(^{2+})</td>
</tr>
<tr>
<td>murexid</td>
<td>red</td>
<td>violet</td>
<td>12 ~ 12.5</td>
<td>Ca(^{2+})</td>
<td>Co(^{3+})</td>
</tr>
<tr>
<td>Tymolftalein</td>
<td>blue</td>
<td>gray</td>
<td>12 ~ 12.2</td>
<td>Ca(^{2+}), Si(^{2+}), Ba(^{2+})</td>
<td>Mg(^{2+})</td>
</tr>
<tr>
<td>Tiron</td>
<td>blue</td>
<td>colourless</td>
<td>2 ~ 3</td>
<td>Fe(^{3+})</td>
<td>Ti(^{4+})</td>
</tr>
</tbody>
</table>

The murexid - ammonium salt of the purple acid (NH\(_4\)H\(_4\)Ind), red calcium complex at pH > 10 transits into the blue-violet anion (H\(_2\)Ind\(^{3-}\)).

Erriochrome black T - sodium salt of 1-(1-hydroxy-2-naftyl azo)-6-nitro-2-naftalensulphon (NaH\(_3\)Ind), wine red complex of ions M\(^{2+}\) with the indicator releases at the equivalence point a blue coloured indicator anion HInd\(^{3-}\).

Fluorexon – \{bis[N,N-di(carboxymetyl)-aminometyl]}fluorescin (H\(_6\)Ind), a yellow-green phosphorescent calcium complex transfers in the equivalence point at pH > 12 to the light pink anion of the free indicator.

Expression of the determined constituent content from the results of titration

- It is necessary to know the stoichiometrical equation of the reaction reagent (A) and determined component (B). \(xB + yA \rightarrow \text{products}, \ \frac{x}{y} = \text{ratio of the number of moles.}\)

- In titration the volume \(V_A\) reagent was consumed and the A with the concentration \(c_A\) (which is given).

- The stock solution of volume \(V\), the quantity \(P\) in titration was pipetted.

\[
\%B = \frac{m_B}{m_{\text{raw}}} \cdot 100 = \frac{n_B \cdot M_B}{m_{\text{raw}}} \cdot \frac{V}{P} \cdot 100
\]

\[
n_B = \frac{x}{y} \cdot V_A \cdot c_A
\]

Example: The calculation of the content Na\(_2\)O (water glass sodium liquid - CSN 653191)
From the initial the water glass is weighed \( m_{w_0} \) (about 10 g) into a 500 ml flask \( (V) \), the \( P \) partition is pipetted, the HCl \( (c_A) \) is titrated to methyl red from a yellow to the pink colour, and the consumption of HCl is \( V_a \).

\[
\% \text{Na}_2\text{O} = \frac{V_a \cdot c_A \cdot 0.0031 \cdot V}{m_{\text{Na}_2\text{O}}} \cdot \frac{1}{P} \cdot 100
\]

The general principles of volumetric analysis

- Titration solutions must be prepared diluted (0.05 M, 0.02 M) to reach an equivalent point using 1 ~ 2 drops of reagent.

- From the reserve solution rather a greater share \( (P) \) is taken, so that the consumption of \( V_a \) is greater, and it is then determined with a minor error.

- The intensity of the solution colour, thanks to the indicator, should be reasonable so that the colour change can be clearly visible.

- We will carry out the titration of the two samples (for comparison).

- We titrate on a white or black background.

- The titration is relatively quick, some reagents are sensitive to e.g. CO\(_2\) from the air.

A summary of the chapter (subchapter)

- Neutralizing the titration.
- Redox reaction.
- Precipitation.
- Complexometry.

Questions for the subject studied

1. What is the division of reactions in volumetric analysis?
2. Explain the nature of neutralisation reaction.
3. Specify examples of indicators for precipitation.
4. Explain the concept of basic substance.
5. Describe the redox reaction.
6. Define precipitation.
7. Explain the concept of complexometry.
8. Write the formula for chelatony III.
9. List examples of indicators for complexometry.
10. Indicate the general principles for the volumetric analysis.
2.3. The methods of spectral (optical) analysis

**Time for study** 240 minutes

**Goal** After studying this section you will be able to
- define spectral methods
- describe the methods of optical spectroscopy

**Lecture**

These methods are qualitative and quantitative.

The essence of spectroscopy is to monitor changes that occur during the interaction of radiation with some substances (absorption spectroscopy), or in subsequent radiation processes for an interaction releasing energy from a reaction with a substance (emission spectroscopy).

The atoms and molecules of substances may be located in different energy states, in the basic condition with the lowest energy, or in an excited state with higher energy. These energy sources are not arbitrary, but they reach only certain values corresponding to certain levels (e.g. the possible points of occurrence). For their transition from an initial to an excited state the difference in energy must be delivered in the form of a quantum \( \varepsilon \).

\[
\Delta E = E_2 - E_1 = \varepsilon = h \cdot \nu = h \cdot \frac{c}{\lambda} = h \cdot c \cdot \bar{\nu}
\]

where
- \( h \) is the Planck constant (6.626 \( \cdot \) 10\(^{-34}\) J.s),
- \( c \) - speed of light in vacuum (2.998 \( \cdot \) 10\(^{8}\) m.s\(^{-1}\)),
- \( \lambda \) - wavelength (m),
- \( \nu \) - frequency (s\(^{-1}\)),
- \( \bar{\nu} \) - wave number (m\(^{-1}\))

From that relationship applies:

\[
\varepsilon \cdot \lambda = h \cdot c
\]

\[
\varepsilon \cdot \lambda = konst.
\]

Therefore, the higher energy of excitation corresponds to a shorter wavelength of radiation, which is absorbed or re-emitted during transition from the excited state to the initial one.
The summary of spectral methods

<table>
<thead>
<tr>
<th>Radiation and wavelength of radiation</th>
<th>The name of analytical method, which uses this radiation</th>
<th>What is changing in the substance</th>
<th>Use</th>
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<td>Mössbauer spectroscopy</td>
<td>The energy changes of nucleus</td>
<td>Information on oxidation degrees</td>
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<td>X-ray radiation 0.01 - 10</td>
<td>X-ray fluorescence analysis (XRF)</td>
<td>The energy changes of electrons at the internal spheres</td>
<td>the chemical composition of substances, identification of components</td>
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<tr>
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<td>infrared radiation 800 nm (0.8 µm) - 100 µm</td>
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<td>The vibration and rotating states of atoms in the bondings change</td>
<td>The detection of functional groups of atoms</td>
</tr>
<tr>
<td>Microwave radiation 100 µm – 1 cm</td>
<td>EPR - electron spin resonance</td>
<td>Orientation of spins of non-paired electrons changes</td>
<td>Information on the structure of substances</td>
</tr>
<tr>
<td>Radio frequency radiation 1 cm - 500 m</td>
<td>NMR - nucleus magnetic resonance</td>
<td>Change in the rotation of cores and spins</td>
<td>Information on the molecules structure, oxidative number</td>
</tr>
<tr>
<td>electron beams (accelerated flow of electrons)</td>
<td></td>
<td></td>
<td>the character of substances surface</td>
</tr>
</tbody>
</table>

Different types of radiation have different energy, and thus their effects on a substance will be different. In interaction with the atoms and molecules the spectroscopy deals with two fundamental processes:

- When the radiation transfers through the analysed substance, a certain part of this radiation with certain wavelengths will be absorbed, while the radiation of other wavelengths will pass through such a substance unchanged. This process is the essence of the **absorption spectroscopy**, in which the degree of radiation absorption and the wavelength is registered.

- In the second case at first energy excitation occurs of the substance (atoms or molecules) using the primary device (flame, electrical spark, laser, etc.). The atoms or molecules then emit - when they return to the initial energy state - a characteristic radiation of certain wavelengths. This process examines the **emission spectroscopy** (again λ and the degree of excited radiation).

λ and a degree of absorption, or emission of radiation is linked to the concentration (element, component) and it is used to determine their content in the sample, i.e. as an analytical method it is qualitative as well as quantitative.

For electron transitions (optical spectroscopy) in atoms and molecules on external sectors the photons of UV and VIS radiation are necessary (i.e. with greater energy).
Optical spectroscopy is therefore divided to:

- Atomic - the substance is in a gaseous state, the sample is dissociated to atoms - and gasified in advance.

- Molecular - the substance is a solution in the form of a specific compound, complex etc. In this compound the atoms of electrons are excited.

The dependence of radiant power on the wavelength = spectrum (the relation of the absorbed power and $\lambda = $ absorption spectrum; the relation of the radiant power emitted to the radiation at $\lambda = $ emission spectrum).

Spectra associated with electron transmissions in atoms (i.e. in gaseous state substances) contain only a limited number of possible energy transitions = bar spectrum. In molecules the different energy transitions of electrons overlap (i.e. in the case of liquid and solid substances, electron spectrum have the character of bends = bend spectrum).

The degree of absorption or electron radiation emission is connected to the concentration of atoms or molecules of a given type, and they are used to determine their content in the sample - quantitative, the chemical analysis of given atoms (either free or bound in the particular type of molecules).

The basic distinction of spectral (optical) analysis methods:

1. The methods of absorption
   a) molecular - colorimetry, photometry, spectrophotometry
   b) atomic - atomic absorption spectrometry (AAS)

2. The methods of emission
   a) atomic - emission atomic spectrometry (EAS)
   b) molecular - molecular emission spectrometry (fluorescent spectrophotometry)

**Molecular absorption spectroscopy**

The basis to establish (qualitatively and quantitatively) the content of a certain cation in a solution is that by adding a reagent so this cation is converted into a certain substance, a certain type of molecule (complexes, compounds, etc.), which will remain in the solution. We determine the difference in the size of radiation power before and after the cuvette, containing the analysed molecules, in a certain quantity of solution. This difference indicates the size of radiation absorbed by the molecules in the solution.

We monitor either the absorption of a whole visible radiation (the whole spectrum of $\lambda$), or by a majority of this monochromatic radiation absorption, from a narrow spectral interval determined from a continuous spectrum.

The way of monochromatization: using filters or the decomposition of the prism or lattice.

When using a visible light (in whole or in part) a solution of coloured substance is often prepared (cation + reagent = colour complex). The intensity of colour corresponds, with the same layer solution (the thickness of the container), to the concentration of the determined cation. The most accurate is the
use of monochrome light with a $\lambda$ absorption maximum (the radiation of wavelength, which is the most absorbed by the coloured complex).

Warning - the substance (complex) in a solution absorbs the wavelength of the additional colour to that one, which is clearly visible to the eye, i.e. we see the least absorbed wavelength, the so-called complementary colour.

Perfectly permeable substances have $A = 0$ and $T = 1$ (100 %), substances which block the radiation have $A = \infty$ and $T = 0$. Absorption depends on the concentration of absorbent molecules $c$, on their properties given by the value of $\varepsilon$ and the width of cuvette $l$.

For the evaluation of constituent content based on the absorption of certain $\lambda$ (with maximum absorption) we shall draw a calibration graph showing the dependence of $A$ on the concentration $c$. Since the partial absorption of a specific wavelength is due to other molecules (e.g. from added chemicals for pH adjustment, masking, etc.), except for the absolute dependency of $A$ on $c$ we can perform the experiment differentially, against the so-called blank test (in the same size cuvette there is a solution of all these chemicals, without the proper sample). Dependence $A = f (c)$ then passes through the start.

Specific methods based on molecular absorption in the visible and UV absorption (due to absorption of energy in the electron leap to the external domains in atoms bind in certain molecular clusters):

- **Colorimetry (VIS)** - the determined cation is in reaction with an appropriate reagent and is transferred to a suitable colour in the solution, and the colour of this solution is compared with a huge range of the same type standards, prepared in different known concentrations. All colour solutions are in the same containers (cuvettes). At the same $l$ and $\varepsilon$ the absorption of light is proportional to the concentration of cation. Example: yellow coloured solution $\text{Fe}^{3+}$ with sulphosalicylic acid in ammonia environment.

- **Photometry (VIS)** - we work in the visible area of the spectrum, so you can compare only the coloured solutions. It is measured visually or by using a photocell of radiation absorption in the same cuvettes, monochrome light is used (after decomposing VIS using filters), and through a colour filter only a certain $\lambda$ can pass.
Spectrophotometry (UV + VIS) - the absorption of monochromatic radiation is measured using photoelectric detectors, direct absorption or transmittance is registered. Monochromatization is done using a prism or lattice. It is measured in cuvettes of a certain thickness, mostly double cuvettes, i.e. directly against the blank test.

Atomic absorption spectroscopy

This method’s name and of all its instrument variants is atomic absorption spectroscopy (AAS).

Any substance absorbs most of such radiation, which it emits itself after energizing (Kirchhoff's law). Its use for analytical purposes is that the atoms of each element in the sample will absorb the light of exact wavelength, which corresponds to the lines of its emission spectrum. Each element is characterised by some $\lambda$ at an interval of 190 - 900 nm, which this component absorbs via the external electrons of free atoms.

The size (level, robustness) of this absorption of specific $\lambda$ is proportional to the concentration of the element in the sample. In order to have the available atoms of elements, which are present in the sample, the sample must be at first in its gaseous state e.g. with or without any flame. Atomization requires a temperature of 2,000 to 3,000 K.

Flamboyant atomizer - a sample in the form of an aerosol is brought into the burner flame where it dissociates to carbon atoms. Burners used are hydrogen-air, acetylene-air, hydrogen-oxygen, and acetylene-oxygen.

Electrothermic atomizer - a graphite furnace with a diameter of several mm, a few millilitres of solution are dosed into it. Heating to about 3,000°C atomization begins.

For the measurement this instrument must contain a light source (radiation) with the values $\lambda$ that must correspond to different elements, for each element a separate lamp is at disposal. It is a hollow cathode lamp: a glass flask filled with neon under pressure, with a cathode from a relevant metal and a tungsten anode. By inserting the voltage there is a discharge occurring, ions $\text{Not}^+$ push the metal atoms out of the cathode metal atoms in the excited state. During deexciting these atoms emit this energy of exact specific $\lambda$. At the same time they pass through a quartz window and pass through the space, into which an atomized sample is sprayed. So if the sample contains atoms of the same component from which the cathode lamp is made, a part of the radiation for the given $\lambda$ values will be absorbed in proportion to the quantity of the element in the sample.

Radiation in the sample passes through the monochromator (prism or lattice), and thus the other $\lambda$ are eliminated, and the intensity of passed radiation $\mathcal{O}$ compared to $\mathcal{O}_0$ is reduced by a proportion absorbed by this element and it is detected by a photomultiplier, it is amplified and registered.

This method is more advantageous than the emission methods to determine various components, because the likelihood of absorption is higher than the emission. The disruptive influence of other atoms is minimal, so it is possible to analyse even very complex samples. This method is suitable for detecting the high and medium concentrations of elements, but also for a trace analysis.

The disadvantage here is the need for a large number of lamps (the sources of radiation), and their number equals to the number of components determined. The price of the instrument is therefore high. It is possible to determine up to 60 different elements.

The rule for its use: first perform the atomic emission analysis (find out which components are present in the sample - quality) and only then using AAS FIXME determine the quantity.
**Emission atomic spectroscopy (EAS)**

The model of a hydrogen atom - there are some "levels" of the possible occurrence of electrons during the excitation of an atom. The energy differences between the various levels are unique for a given element and therefore they are characteristic. This means that even the wave lengths of spectral lines (i.e. radiation of energies in retrospect flashover) of the atoms are characteristic and they are determined by a relevant transition from a level with higher energy to the level with less energy.

\[
\lambda = \frac{h \cdot c}{E_m - E_n}
\]

The basis for a qualitative emission analysis is the relation \( \lambda = f(Z) \), where \( Z \) is the atomic number of element.

Emission spectrometry is a method of the quantitative and qualitative analysis of substances, based on the examination of radiation that these substances are emitting. For that to happen, atoms in a sample must be first changed to the excited state. The emitted radiation is a polychromatic, since it is created by leaps of external electrons from the excited levels to the basic ones. From the point of qualitative analysis the wavelengths (the lines of the spectrum) are the most important, they are formed by a transition between the first excited and the basic level (marked lines \( \alpha \) in the relevant series, i.e. on a specific basic level of \( H_\alpha \)) that are marked as resonance lines or also the last, because with the gradual reduction of the concentration in the sample they are disappearing from the spectrum, as the last ones. From the Heisenberg uncertainty principle it is clear that the position of a certain electron and its speed cannot be determined accurately at the same time, and therefore also the inaccuracy in determining its energy exists together with inaccuracies of the time determination. This explains the certain natural width of spectral lines. Tabulated values are related to the peak position of spectral lines. The profile of a spectral line is not constant, but it depends on the awaking conditions.

Information about the wavelengths of spectral lines emission arranged in accordance with certain criteria are listed in the tables. The most frequently tables of the last lines are used, but also other ones, mostly sorted according to the components.

Spectrometers, i.e. the apparatus used in optical atomic emission spectroscopy, have the following functions:

- excitation source (atomizer),
- device to generate spectrum (isolate \( \lambda \) ),
- the detector of radiation,
- a device to process the measured data and determine the analytical parameters.

The arising power supply provides electrical or thermal energy to transform the sample from a solid or a liquid state into a gaseous, to dissociation, atomization, and to attract the electrons in atoms.

The principle of this method is to examine the emission radiation that arises when the sample is brought to the gaseous phase, and thus atomized. Present atoms may be excited using flame, electrical spark, arc, laser, or today by mostly plasma (IPC - inductively coupled plasma, consists of argon, the necessary energy is supplied by a radio frequency field). The energy of the flame is low, so it is sufficient to excite the elements with the lowest ion potentials (alkaline metals, alkaline earth metals).
Radiation transmits (emits) all present excited elements simultaneously, so the radiation is a polychromatic. For its decomposition we use either a prism or lattice optical radiation (so-called dispersive components).

The entire device to generate the spectrum - the determination of individual spectral lines contains also interstices determining a certain part of the whole polychromatic spectrum.

Decomposed radiation is captured e.g. on the photographic plate and thus an emission line spectrum occurs, consisting of a number of vertical lines corresponding to the radiation of individual elements (now displayed on computer). Each component has a unique spectrum, its lines have a certain wavelength. The information obtained is then compared with the tabulated data (spectral tables). The agreement in the lines positions (value \( \lambda \)) of the spectrum with the data on elements is qualitative evidence of an element’s presence. The quantity (concentration) of a component is given by the intensity of lines - quantity.

According to the method of detection there were the older equipment called spectroscopes - observation of the spectra by the eye, without any registration. Now, there are the spectrographs - with a recording option, for the samples of the same types we use quantometers. In a quantometer there is a row of exactly set slots, which shield radiation of the appropriate lines in the analysed elements. Behind the slots there are photomultipliers, which amplify the luminous flux. The signal is electrically processed and evaluated directly in the data of element concentration. Thus, it is possible to monitor and evaluate up to 25 elements in about five minutes. The equipment is very expensive, and suitable for a large series of samples.

For most elements the EAS method can prove the presence at the level of \( 10^{-3} \) to \( 10^{-4} \) hm %. This method is one of the most sensitive physical methods to detect the presence of trace element contents in different materials (quality). This method is not applicable for the quantitative analysis of macro constituents (other methods are more accurate).

**Emission spectroscopy of molecules**

The molecules whose atoms are in an excited state are returning to the basic state (their electrons) after some time, and they emit radiation. The difference of energy in these two states is released in the form of radiation. By monitoring this emitted radiation we obtain information on the electron states of molecules. Luminescent spectroscopy deals with studying the processes associated with this emission of radiation.

Luminescent radiation varies according to how the molecule got into the excited state. If the molecule absorbed radiation, its emissions in their reverse transition are called photoluminescence and phosphorescence. The molecule can get into an excited state by a chemical reaction, the product of this chemical reaction in its excited state, and the transition to a basic state is associated with the emission of radiation - this is called chemiluminescence. When this process is taking place in biological systems, it is a bioluminescence, by the effect of an electric field it is called electroluminescence, etc.

If the energy is derived from this excitation (i.e. by absorbing energy) it emits completely in return to the molecules of the basic state, for it is the characteristic radiation and this phenomenon is called fluorescence. However, the molecule may get from the excited state into the so-called triplet state via non-radiation transition and only the subsequent transfer of a molecule into the basic state is associated with the emission of radiation, the so-called phosphorescence. The phosphorescence of radiation has higher wavelengths, and its radiation energy is very small.

For the compound to radiate fluorescence it is necessary for it to absorb and then emit in the visible or long-wave UV region. The majority of aliphatic compounds do not meet these conditions. Most fluorescent substances can be found among organic aromatic compounds. A large group of fluorescent
compounds are complexes of organic molecules with metal ions (by creating a complex with metal ions the rotation of molecule parts is reduced and the system shows strong fluorescence). This phenomenon is used in analytical chemistry to identify and determine various ions, but also in the titrations, where the appearance or disappearance of fluorescence indicates an equivalent point. For example Al, Be, Cs, In, Zr, U, Th etc. They form strongly fluorescent complexes with reagents such as rodamin, 8-chynolinol, etc. A method of calibration curves is used. Very small limits of determination, up to $10^{-12}$ g.ml$^{-1}$ are important. In biochemistry, some hormones are determined this way, as well as enzymes, alkaloids, etc. On the basis of the bioluminescent responses some bacteria in water or in foodstuffs are determined.

A summary of the chapter (subchapter)

- Spectral methods.
- Molecular absorption spectroscopy.
- Lambert-Beer's Law.
- Absorbance. Transmittance.
- Atomic absorption spectroscopy.
- The emission of atomic spectroscopy.
- The emission spectroscopy of molecules.

Questions for the subject studied

1. Name the methods of spectral analysis.
2. Explain the difference between absorption and emission spectroscopy.
3. How is the optical spectroscopy divided?
4. Describe the method of molecular absorption spectroscopy.
5. Define the Lambert-Beer's Law.
6. Describe the method of atomic absorption spectroscopy.
7. Describe the method of atomic emission spectroscopy.
8. Explain the emission spectroscopy of molecules.
3. The methods of phase analysis

3.1. The infrared spectroscopy (IR - infrared)

Time to study 60 minutes

Goal After studying this paragraph you will be able to

- define infrared spectroscopy
- describe infrared devices

Lecture

Infrared radiation is such that it is perceived through the bondings in molecules. These bondings may cause rotary or vibration movements. It is used to study the structure of molecules (what atoms are present in a substance). The molecule changes its vibration and rotary states, these states can be monitored independently of electron transitions (changes in the states of molecules are caused by the action of atom electrons, but these changes are observable without any knowledge of events at the level of atoms). Measured values of vibration and rotary energy are linked to the strength of chemical bonds and also to the molecular geometry and masses of nuclei, i.e. of a molecular structure.

This vibration can be illustrated using the example of two balls linked by a spring→ atoms of molecules linked by a bond:

- IR radiation first causes a stretching of links (a spring)
- The binding energy acts against the direction of "stretching" and will force these atoms to return; they will not return to their original position but molecules are getting closer than they were at the beginning
- The oscillation (vibration) movement of atoms forming a molecule occurs.

Infrared spectroscopy belongs to the group of non-destructive analytical methods, where the sample analysed is not damaged, and yet it provides information about its composition. The values obtained by vibration energy are linked to the strength of chemical bonds and also to the molecular geometry and masses of the nuclei, i.e. of the molecular structure.

The basis of infrared spectroscopy is the interaction of infrared radiation with the analysed mass, when in the case a photon is absorbed by the studied matter we are talking about the absorption of infrared spectroscopy, and in the case of radiation of this photon we can talk about emission infrared spectroscopy. Infrared radiation is an electromagnetic radiation in the range of wave numbers (the most commonly used unit in the infrared spectroscopy is the wave number, which is linked to the wavelength by relation \( \bar{\nu} = 1/\lambda \) and with frequency of \( \bar{\nu} = V/c \)). Infrared radiation therefore follows visible radiation on one hand and microwave radiation on the other.
Its analytical output is the infrared spectrum that is the graphical output of the functional dependence of energy, mostly expressed in transmission percentage (T) or in the absorbance units (A) on the wavelength of incident radiation.

The quality is the detection of peak presence, the quantity is the size of peak.

The infrared device:

- Source of infrared radiation - the source is the heated solid substance (most frequently a Nernstov lamp = heated rod ZrO₂, or Globar lamp = rod from SiC).

- The cuvette for sample - samples may be gaseous, liquid, or solid. Solid samples must be either very diluted, or only a thin layer is used.
  - Very diluted sample = preparation of tablets from the powder sample and KBr in 1:100 ratio.
  - An emulsion of the powdered sample and oil is prepared, spread with a thin layer on a slide.
  - The sample is melted and used to make a thin layer on the slide.

- Monochromator - a device that decomposes radiation and selects the requested wavelength.

- The detector of radiation which has passed through the sample.
  - Photocells - operate on the principle of a thermocouple, and monitor the temperature difference.
  - Bolometers - thermoresistor.

- The registration device - the record is linear, intensity T shall be divided into three groups.
  - Strong zones (s = strong), T > 80%.
  - Medium zones (m = medium), T = 40 - 80%.
  - Weak zones (w = weak), T < 40%.

∑  A summary of the chapter (subchapter)

- The infrared.
<table>
<thead>
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<th>Questions for the subject studied</th>
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<tr>
<td>1. Redefine infrared radiation.</td>
</tr>
<tr>
<td>2. Describe what infrared is.</td>
</tr>
</tbody>
</table>
3.2. X-ray diffraction using XRDA analysis

**Time for study** 300 minutes

**Goal** After studying this paragraph you will be able to
- define the crystalline structure of substances
- define equidistant planes
- define the emergence of x-ray radiation
- define the conditions of amplifying x-ray radiation

**Lecture**

X-rays radiation is a high-energy electromagnetic radiation with a wavelength of $10^{-10}$ Nm = 1 Å (angstrom). We use it to identify changes that arise in the inner sphere, i.e. the internal electrons that are very close to the nucleus.

The methods of x-ray analysis based on diffraction are used to determine the mineralogical (phase) composition of all substances that have a crystalline character.

X-ray diffraction analysis is based on two principles:
- the crystallographic arrangement of substances,
- the interaction of x-ray radiation with particles forming the crystal lattice.

The crystalline substances have regularly placed atoms in the direction of three axes. The size of vectors is known as $\vec{a}$, $\vec{b}$, $\vec{c}$ from the departure node, and also the size of angles $\alpha$, $\beta$, $\gamma$. This means that we have six fundamental values and those describe a regular crystalline structure.

The shape that characterises the substance is called the elementary cell, and these are then repeated periodically in all directions. Each crystal shows a set of parallel planes, and interlaced lattice crystal planes in different directions. The simplest arrangement is a cubic system (Figure 2).

Equidistant plane, i.e. the plane parallel and equally apart, are identified by known Miller indices (h, k, l) which indicate the position of these planes in a spatial lattice. The distance of these planes is marked d, and it is supplemented if necessary by Miller indices d<sub>hkl</sub> (e.g. d<sub>001</sub> - basal plane) (Fig. 3).
Distance between planes.

Each elementary cell can be interspersed by a series of equidistant planes that their values of \( h, k, l \) are small whole numbers. The least number of planes can be interspersed among a cubic system. Each crystalline substance in the world has a different set of values for interplanal distances \( d_{hkl} \) and this is unique for each substance, and meets the condition that \( d \) are small whole numbers. From these planes an x-ray will be reflected.

The emergence of x-ray radiation

X-ray radiation is produced in x-ray tubes (Coolidge tubes). These are tungsten cathodes and an anode from copper, located in the flask with a vacuum (Fig. 4). Between the anode and cathode there is large voltage applied (60,000 eV). By heating the fibre the electrons are pushed away from the cathode, speeded up by the high voltage, they hit the anode, where they are stopped. The electron hits the Cu anode in its internal electrons (e1, Fig. 5) from some lower energy level of an atom (energy level K, Fig. 5) and this flies out into space. An electron from a higher sphere takes its place (e2, Figure 5). During the jump of electron there is a photon emission, which comprise x-ray radiation, with the energy of value that the electron lost by a jump from the more distant and energy higher level to a closer, energy lower level. This radiation has an exact wavelength \( \lambda = \hbar \cdot \nu \) marked Cu \( K\alpha = 0.15418 \) m = 1.5418 Å. Thus we have prepared a monochrome (only with one wave length) x-rays radiation (if the Cu anode is coated with a thin layer of e.g. Co, we get Co \( K\alpha \)). The resulting radiation is directed to the sample and in certain circumstances the radiation will increase.

The figure shows the three neighbouring planes with interplanar distance \( d_{hkl} \). The monochrome beam of x-ray radiation hits the crystal at an angle \( \theta \) toward these planes. The amplification of diffracted rays interference occurs only between those two rays that:

- are parallel,
- their paths will vary by precisely \( \lambda, 2 \cdot \lambda, 3 \cdot \lambda, \) etc., i.e. the path difference must be generally \( n \cdot \lambda \), where \( n \) is a whole number,

The first condition requires that the common angle of the two beams’ dispersion was equal to the angle of impact \( \theta \) of the original beam. The second condition requires using the Bragg equation:
The amplification of diffracted rays of interference on crystal atoms.

Using the Bragg equation we can be derive (Fig. 7):

\[ n \cdot \lambda = 2 \cdot d_{hkl} \cdot \sin \theta. \]

For each series of planes interlaced in a specific crystal, there is a single angle \( \theta \), during which the radiation (diffraction) is amplified and the Bragg condition met. The wavelength of incident radiation is chosen so that the length of one wave matches the order interplanar distances in the crystals. It will be \( n = 1 \).

For the identification of a powdered sample the Bragg-Brentan layout is used (Fig. 8). Each present mineral after the execution of analysis shows its diffractions, irrespective of other minerals present.
The principle of Bragg-Bretan layout: 0 - axis of diffractometer, 1 - x-ray tube, 2 - sample, 3 - computer pulses, 4 - recorder, 5 - printer.

X-ray diffraction XRDA analysis method is only qualitative. The quantity can be determined only under certain specific conditions.

A summary of the chapter (subchapter)

- The elementary cell.
- Equidistant planes.
- X-ray radiation.
- Bragg's equation.
- Diffractometer.

Questions for the subject studied

1. On which principles is x-ray radiation based?
2. Describe the crystalline structure of substances.
3. Explain the emergence of x-rays.
4. Explain the conditions to amplify x-ray radiation.
5. Derive the Bragg equation.
6. Describe a diffractometer.
3.3. X-ray fluorescence spectrometry (XRFS)

Time for study 60 minutes

Goal  After studying this paragraph you will be able to
• define the method of XRFS
• describe the principle of the XRFS method

Lecture

It is a method of chemical analysis not a phase analysis!

It is a qualitative and quantitative method. We use it to determine the presence of elements in a sample. (Only the elements from Na higher, lighter elements cannot be determined using this method). Thus the result is an analysis of elements, which is to be counted in oxides.

The source of radiation is the x-ray tube. Primary radiation strikes a sample from which the secondary x-ray radiation is expelled. Secondary radiation is decomposed according to a) wavelengths or (b) the energy of photons.

A) Secondary radiation using the collimator is guided to a beam of parallel rays that hit the rotating dispersive crystal where, after meeting the conditions of the Bragg equation, diffraction radiation takes place.

Diffraction occurs with a correct rotation of the crystal against the lines parallel to the x-ray beams. This angle of rotation is unique due to the nature of the substances to be analysed. The analysed substance (atom) emits radiation whose spectrum is unique due to the limited possibilities of electron "flashovers" at the internal orbits of an atom. Reflected radiation is routed to the detector that evaluates these recordings.

B) Instrument operating on the evaluation of photons energy: instead of a dispersion crystal as secondary x-ray radiation a silicon semiconductor is used. Current pulses recorded in a silicon semiconductors correspond to the photons of secondary x-ray radiation.

A tool for XRFS measuring consists of sources of monochrome x-rays radiation. Radiation is sent on a powder sample consisting of different atoms. X-ray radiation with a certain probability hits some specific atom of this sample, so that the internal electron is blown out. Its place is taken by an electron from a higher energy level, and the difference in energy emits as x-ray radiation of accurate $\lambda$. Similarly, the radiation hits other atoms in the sample, and thus we get various values of x-ray radiation with precise wavelengths. All radiation resulting this way is directed to a crystal with known value $d_{hkl}$ and we change only the angle $\theta$ (the angle at which the radiation beam is sent on the crystal). Then the Bragg equation is valid, when at a known angle $\theta$ and common values of $d_{hkl}$ we can determine the values $\lambda$. 

Qualitative analysis
- Based on the assumption that each element is characterized by a set of lines with precisely defined wavelengths. This is analogous to the emission spectral method, but contains less lines (and a smaller number of flashovers at internal orbits). Diffracted lines will be marked using Greek alphabet letters.

Quantitative analysis
- the intensity of lines is linearly proportional to the concentration. The concentration is determined on the basis of comparing the record with the calibration curves, or a mathematical calculation is used.

A schematic representation of XRFS equipment

A summary of the chapter (subchapter)

- The equations of the Bragg-Bretan layout.
- The principle of XRFS.

Questions for the subject studied

1. Explain the principle of the XRFS method.
3.4. Methods of optical and electron microscopy

Time for study 300 minutes

Goal  After studying this paragraph you will be able to
- define the concept of an optical system
- describe the distinctive character of an optical system
- define electron transmission microscopy
- define raster electron microscope

Lecture

Microscopy in the area of visible radiation (optical microscopy) is a suitable method to study textures, structure, and phase composition.

The optical system is given by our ability to distinguish. The human eye can, under suitable lighting, distinguish two points that are apart from each other some 0.2 mm. If the distance is less, points merge into one. This distance is called the distinctive ability, and it is the most important characteristics of a microscope.

Modern optic microscope (LM - Light Microscope) has a magnification of about 1000x and allows for the eye to distinguish between two objects distant from each other about 0.0002 mm. With continuing efforts to achieve a better resolution it was found that the resolution of a microscope is not only limited by the number and quality of the lens, but also by the wavelength of light used to light the object. The use of radiation with a shorter wavelength (blue or UV radiation) has led to a small improvement, to the immersion of preparation and the front lens into a liquid with a high refractive index (oil) led to some further small improvement; but both of these measures improved the resolution ability of just under 100 nm (one nanometre is one millionth of millimetre, i.e. $10^{-9}$ m).

In 1920 it was discovered that the accelerated electrons in a vacuum behave in the same way as light. They move along a straight line and have the wavelength of approximately 100,000x less than light. Furthermore, it was found that the electrical and magnetic field is affecting them in the same way as lens and mirrors affect visible light. Dr. Ernst Ruska of Berlin University combined these phenomena in 1931 and built the first transmission electron microscope (abbreviated TEM). Currently five magnetic lenses are used in imaging system, reaching a resolution of 0.1 nm at a magnification of one million.

Transmission electron microscopy (TEM)

Electron microscopy builds on optical microscopy in the studies of microstructures at a magnification and resolution that is beyond the capabilities of an optical microscope.

A transmission electron microscope is schematically shown in Figure 10. The optical system consists of an electron nozzle emitting a flow of electrons, and of several electromagnetic lenses, which the electron beam passes through, and which are powered by DC voltage of variable values, allowing
different degrees of zoom. Between the lenses a chamber with a preparation is placed, through which the electrons pass, and the image of preparation is then transmitted after various deceleration of its kinetic energy to a fluorescent light hood. The entire path of this electron is in a vacuum. The reason for this is that the electrons are easily stopped, can deviate or bounce after the impact on matter (an electron is almost 2000x smaller and lighter than the smallest atom). For this reason the preparation must be also very thin, so that the electrons may penetrate it well.

Diagram of a transmission electron microscope

The higher the acceleration voltage, the greater the speed of electrons. Electrons sped up by 80 kV voltage travel at speeds of 150,000 km per second, which is half the speed of light. The speed of these electrons sped up by 300 kV is already 230,000 km per second, which is about two thirds the speed of light.

If the preparation for the TEM is not slim, electrons would stops in it and no picture would be obtained. A typical electron beam has a current of about 1 picoamper (10⁻¹² A). One amp corresponds to the charge of 1 coulomb per second. An electron carries a charge of 1.602 × 10⁻¹⁹ C. The preparation is therefore hit by about 6 million electrons per second.

Samples for TEM usually have a thickness of 0.5 μm or less. The higher the acceleration of voltage in the electron nozzle, the faster the rate of electrons and the greater may be the thickness of the preparation. The TEM can be used in any scientific discipline, where it is necessary to study the structure of a sample up to the atomic level. The preparation must be sufficiently stable and small (approximately 3 mm in diameter), so that it can be inserted into the vacuum tube of the microscope.
For samples for TEM there shall be prepared:

- ultra-thin slices (from biologically soft tissues),
- the carrier foil,
- the technique of transfer

The majority of preparations is not damaged by bombarding electrons during the whole process of analysis. When the electron hits the preparation many phenomena can occur:

- Some of the electrons are absorbed, depending on the thickness and composition of the preparation, and this causes the so-called amplitude contrast of image.
- Other electrons are spread over the small angles depending on the composition of the sample, and this causes the so-called phase contrast of image.
- In crystalline preparations the electrons are diffused into various angles depending on the crystal structure, and this causes the so-called diffraction contrast of the image.
- Some of the incident electrons are reflected (called reflected electrons).
- The incident electrons can cause the emission of electrons in the preparation (and these emitted electrons are called secondary electrons).
- The incident electrons may cause x-ray beam emission in the preparation, as their energy and wave length depends on chemical elements contained in the preparation.
- The incident electrons may cause the emission of photons (or light) in the preparation, and this is called cathodoluminescence.
- Electrons which have lost a quantum of energy in interaction with the preparation may be detected by a spectrophotometer measuring the loss of energy, which is analogous to a prism in light optics.

In standard TEM the first two phenomena contribute to the formation of a normal TEM image in the non-crystalline (biological) preparations, while for crystalline preparations they are the most important factors forming the image phase and diffraction contrast.

**Raster (scanning) electron microscope (SEM)**

The SEM, as well as the TEM, consists of a tube with electron optics, a vacuum system, and electronics. The chamber for the preparation is greater, as the SEM technique does not limit the size of preparation in any way. All parts of SEM usually form a single unit.

The electron nozzle at the top part of this tube emits a beam of electrons that is focused on a small flat area on the surface of the preparation, whose diameter is less than 4 nm. The beam passes in the orthogonal grating (spacing) on the surface of the preparation. In addition to other phenomena associated with its impact on the surface of the sample the incident electrons are causing the emission of secondary electrons (SE). These are registered by a special detector.

Five phenomena, for the impact of an electron into the preparation, referred to in the TEM, are used for SEM:

- The sample emits secondary electrons (SE - image of topography).
- Some of the primary electrons are bounced (reflected electrons BSE - image composition).
- The electrons are absorbed by the sample.
- The sample emits x-rays.
- The sample sometimes emits photons of light.

All these phenomena are related, and they are all dependent on the topography (the shape of surface) of the sample, the atomic number, and the chemical state of a sample. The number of backward reflected electrons, the secondary electrons, and the absorbed electrons at each point of the sample depend on the sample shape of the surface much more than on the other characteristics. For this reason, these three phenomena are mainly used to display the surface of a sample.

The SEM is used everywhere where the information on the sample surface is required. Many samples can be placed into the chamber of a microscope without any previous treatment. If the sample contains any volatile component (e.g. water), it is necessary to drain it first. Non-conductive samples are coated with a thin conductive layer of approximately 10 nm).

The main differences between the TEM and SEM (Fig. 13)

- A beam of electrons in the SEM is not static as in the TEM - with the electromagnetic field of raster coils a beam is diffracted, so that it passes line by line after an extremely small flat surface on the surface of the preparation.

- Acceleration voltage in the SEM is much smaller than in the TEM because electrons do not have to penetrate the preparation, in the SEM it has values in ranging from 200 to 30,000 V.

- Preparations need no complex preparation.

The comparison of a transmission and raster microscope.

1 - the source of electrons, 2 - electron beam, 3 - preparation (thin), 4 - vacuum, 5 - luminescent hood, 6 - deflection coils, 7 - detector, 8 - monitor, 9 - preparation (very thick).
A summary of the chapter (subchapter)

- The equations of the Bragg-Bretan layout.
- The distinctive ability of optical system.
- Transmission electron microscopy.
- Raster electron microscopy.

Questions for the subject studied

1. Derive the relation for the wavelength of an electron beam.
2. Define the distinguishing ability of an optical system.
3. The principle of the TEM method.
4. Samples for TEM.
5. What phenomena may occur during the impact of electrons in TEM?
7. What phenomena may occur during the impact of electrons in SEM?
8. The differences between the SEM and TEM methods.
3.5. The methods of thermic analysis

**Time for study** 300 minutes

**Goal** After studying this paragraph you will be able to

- describe the methods of thermal analysis
- define direct thermal analysis
- define differential thermal analysis
- describe the method of thermogravimetry
- define the method of DTG
- describe the method of DSC

**Lecture**

The methods of thermic analysis are one of the major sources of information on the properties of solid substances. Generally, the thermal analysis indicates a set of methods to measure certain physical properties of a substance, such as the functions of temperature, while the analysed substance is exposed to a known thermal mode. These methods are used primarily for identification and qualitative analysis.

The division of the methods for thermic analysis (TA) is shown in the following table.

<table>
<thead>
<tr>
<th>Measured feature</th>
<th>The basic techniques</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>Thermogravimetry</td>
<td>TG</td>
</tr>
<tr>
<td></td>
<td>isobaric determination of weight changes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>detection of gas released</td>
<td>EGD</td>
</tr>
<tr>
<td></td>
<td>analysis of the gas release</td>
<td>EGA</td>
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<td></td>
<td>emanational thermic analysis</td>
<td>ETA</td>
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<tr>
<td>temperature</td>
<td>direct thermic analysis</td>
<td>DTA</td>
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<tr>
<td></td>
<td>differential thermic analysis</td>
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</tr>
<tr>
<td>enthalpy</td>
<td>differential scanning calorimetry</td>
<td>DSC</td>
</tr>
<tr>
<td>dimension</td>
<td>thermodilatometry</td>
<td>TD</td>
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<tr>
<td>mechanical characteristics</td>
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<td>acoustic characteristics</td>
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<td>magnetic characteristics</td>
<td>termomagnetometry</td>
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</table>
Differential thermal analysis (DTA)

DTA is a dynamic, heat-analytical method based on the measurement of differences between the tested and inert temperature, when a standard sample is simultaneously heated at a constant speed in a furnace. The heat-coloured reactions in the resulting curve $\Delta T = f(T)$ show their maximum and minimum values. The temperature for DTA is measured with a thermocouple. The temperature difference is measured with a thermocouple in a so-called differential connection.

For the recording of the thermal effect the total quantity of released or absorbed heat is not crucial, but the amount of heat that is released per time unit $dQ/dt$ is. This measure also determines the sensitivity of a device.

In the description of the DTA curve these concepts (fig. 18) are used:

- The base line (zero line) - a part of curve, where it is approximately valid that the temperature difference $\Delta T = 0$ (sections AB, DE).
- The anomaly or peak - a part of curve that is moving away and returning back to the base line (section BCD).
- Endotherm - deflection in which $T_{uz} < T_r$, and thus $\Delta T < 0$.
- Exotherm - deflection in which $T_{uz} > T_r$, and thus $\Delta T > 0$.
- The width of deflection - the temperature or time interval between the point of deflection and the point of return to the base line (points B and D).
- The height of deflection - a part of perpendicular running on a thermal or time line, which is defined by the interpolated base line and the maximum displacement (CF).
- The area of deflection - an area delimited by the interpolated baseline and deflection (BCDB).
- Point G corresponds to the intersection of a tangent to the base line before the effect and the tangent to the steep part of the effect, and represents the construction of a temperature point for the effect $T_0$.
- Point C corresponds to the peak of effect and temperature $T_m$.
- Point D corresponds to the end of the effect, i.e. the temperature point $T$. (Its structure is in the case of round curve transition similar to the G point.)

Schematized DTA curve with the evaluation of the characteristic points of effects.
DTA curves can influence both the design and layout of the apparatus, as well as the measurement methodology or the properties for the substances measured. The position of effects on this curve may be affected mainly by the heating speed, the quantity and dimensions of the samples, the compaction of samples and the atmosphere in the furnace.

The sample and reference material are placed into the metal or ceramic crucibles, which are placed in a heated area openly, or they are located in a solid block. In addition to the size and shape of crucibles the thermocouple locations are also important for the recording sensitivity. The wells of thermocouples are either in direct contact with the sample and the reference substance, or in external contact with crucibles.

Faster heating causes an increase of temperature difference at the peak temperature of effect $T_m$. Particularly significant is that there is a result in reactions accompanied by weight changes, when the depth and area of this effect increases, and the width of the effect is reduced.

More of the sample increase the temperature of peak effect ($T_m$), worsening the readability of neighbouring effects. The compaction, the tamping of a sample increases its thermal conductivity, but worsens any gas diffusion of samples.

The standard must be an inert substance with a similar coefficient of thermal conductivity, the same as of the sample. The most frequently used is the calcined Al$_2$O$_3$, kaolin, MgO, or quartz glass.

**Thermogravimetry (TG)**

It is a quantitative method which monitors the change in the mass of a sample as a function of temperature, while the analysed substance is exposed to a controlled temperature mode.

There are two types of waves:

a) The thermo-gravimetric curves TG express weight change depending on the linearly changing temperature (fig. 22), expressed by $m = f(T)$.

b) The differential thermo-gravimetric curves DTG express the relation of the rate changes in the mass of a sample on the temperature, according to $\frac{d(\Delta m)}{dT} = f(T)$. Using the DTG curve it is possible to evaluate the temperature intervals of weight changes, recorded for the primary curve TG.

![Diagram](https://example.com/diagram.png)

A schematic representation of thermo-gravimetric curves TG. Sections AB and CD are parts of the TG curve, where there is no change in the mass of the sample. Section BC represents the change in the mass of the sample. Point B indicates the temperature $T_1$ at the beginning of the effect and the point C the temperature $T_2$ at the end of the effect.
The TG curve records the sum decreases of sampled mass during heating. The Y-axis is in this case the axis of mass, whose scope can be preselected according to the expected total loss. The interval of mass change is determined from the DTG curve. The maximum of DTG curve corresponds to the inflection point of the TG curve. This provides information about the size of weight changes in the sample and about the temperature interval in which these changes occur; at the same time about the time duration of the process characterised by relevant mass change.

The results of TG measurements are used to assess the thermal degradation or vice versa the fusion of substances, or eventually the representation of these phases, etc.

The advantage of the DTA and TG methods is the possibility of the qualitative and quantitative determination of mineralogical composition in certain analysed substances. The disadvantage is the fact that some minerals cannot be identified using this method and that not all the changes, taking place in this reaction, are accompanied by mass change.

**Differential scanning calorimetry (DSC)**

Also called enthalpic thermic analysis. It is a method by which the difference of electrical power input is measured, which is supplied to the isothermic heating of a sample and reference material as a function of temperature. The analysed substance and the reference sample must be subjected to the same temperature programme. The temperature, and also the temperature difference between the sample and reference material, being the basis for the regulation of electrical power input, is measured by platinum resistance thermometers.

DSC is a method in which the thermal characteristics of a sample exposed to the temperature programme are examined. The sample is heated or cooled by a defined speed together with the sample control, which is the selected reference material. The signal associated with the phase change in the sample is then caused by the actual temperature difference of the sample and reference, which the instrument immediately tries to compensate for. This way there can therefore be evaluated the melting point, the temperature of glass transition, various types of crystallisation, the heat capacity, and the temperature of degradation.

A very small amount of a sample (mg) is used for measurement, they are placed on metal foils and measurement is performed at high temperatures of heating (up to 80°C.min⁻¹).

The DSC method is used to measure isobaric thermal capacity, the enthalpy of phase transformations, to assess the purity of substances, etc.

Differential scanning calorimetry is one of the most widely used methods of thermic analysis. In comparison with the other methods of thermic analysis DSC is probably the most universal to use, and can analyse the solid and liquid samples in a very wide range of temperatures, and therefore it belongs to the standard equipment of most laboratories.

There are two basic types of DSC analysers, namely:

1. The differential scanning calorimetry with compensated power input - based on two identical calometric cells, one for the reference and the other for the analysed sample. If in an analysed
sample there is no activity (for a reference sample we do not presuppose any activity when analysing the temperature range), so the two samples are heated at the same speed according to the specified temperature programme. If in a studied sample endothermic activity takes place, its temperature begins to lag behind the temperature programme, or behind the temperature of the reference sample. At such a moment the supply of energy into the sample is increased and thus its temperature increases up to the temperature level of the sample reference. In the event that the exothermic activity takes place, the temperature of an analysed sample is higher compared to the reference sample, and then the studied sample receives less energy, in order to align their temperatures. The compensation of power input helps to maintain identical temperatures between the two samples. This arrangement allows both very sensitive and very rapid changes in temperature, and last but not least, it is appropriate to carry out isothermal activities.

2. The differential scanning calorimetry with the heat flow - reference and analysed sample are located on separate temperature sensors in the same calometric cell, interconnected by a temperature bridge. With a change in temperature in an analysed sample caused by exothermic or endothermic activities, which causes the temperature difference between the two samples, this temperature difference is recorded as a heat flow between them and it is converted to an energy equivalent, so that the output from the two types of analysers is analogous and mutually comparable.

The output of differential scanning calorimetry is the amount of energy that has to be supplied into the system, whether it is a reference or analysed sample. Graphically it is recorded in the form of DSC curves, where we display energy (in mW units, which corresponds to mJ/s) depending on the temperature (or eventually on time).

Example of DSC curves.
Methods of thermal analysis.
Direct thermal analysis.
Differential thermal analysis.
Thermogravimetry.
Differential thermogravimetry.
Differential scanning calorimetry.

Questions for the subject studied

1. Define the methods of thermal analysis.
2. Explain the principle of DTA.
3. Describe the DTA curve.
4. Explain the principle of the TG method.
5. What is the principle of the DSC method?
6. What types of DSC exist?
Literature

The literature that can draw you to further studies


