

UV-VIS SPECTROPHOTOMETRIC DETERMINATIONS OF SELECTED ELEMENTS IN MODELLED AQUEOUS SOLUTIONS

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Abstract

For the simulation of natural (e.g. sorption, desorption, degradation) or technological processes (e.g. removal efficiency, influence of various parameter as pH, Eh or ionic strength of the solution on the process) are frequently used solutions of compounds, which are relatively readily determined in the investigation medium. Most often compounds studied as model elements are toxic metals (e.g. Cr, Co, Ni), a wide group

of organic compounds are represented by organic dyes (e.g. Methylorange, Methylene blue, Congo red). These substances can be easily determined by UV – VIS spectrophotometric methods. The aim of this paper is to describe the common procedures for selected chemical elements determination in modelled aqueous solutions using UV-VIS spectrophotometric methods.

Key words

spectrophotometry, chromium, nickel, copper, cobalt, aluminium, arsenic, iron, manganese, magnesium, calcium, strontium

Introduction

Spectrophotometric techniques are used to measure the concentration of solutes in solution by measuring the amount of light that is absorbed by the solution in a cuvette placed in the spectrophotometer. Spectrophotometry takes advantage of the dual nature of light. Namely, light has:

1. a particle nature which gives rise to the photoelectric effect,
2. a wave nature which gives rise to the visible spectrum of light.

The spectrophotometer can measure the amount of light (of certain frequency) transmitted or adsorbed by the solution. This light that has not been absorbed by the solution in the cuvette, will strike the phototube. The photons of light that strike the phototube will be converted into electrical energy. This current that is produced is very small and must be amplified before it can be efficiently detected. The signal is proportional to the amount of light which originally struck the phototube and is thus an accurate measurement of the amount of light which has passed through (been transmitted by) the sample. [1]

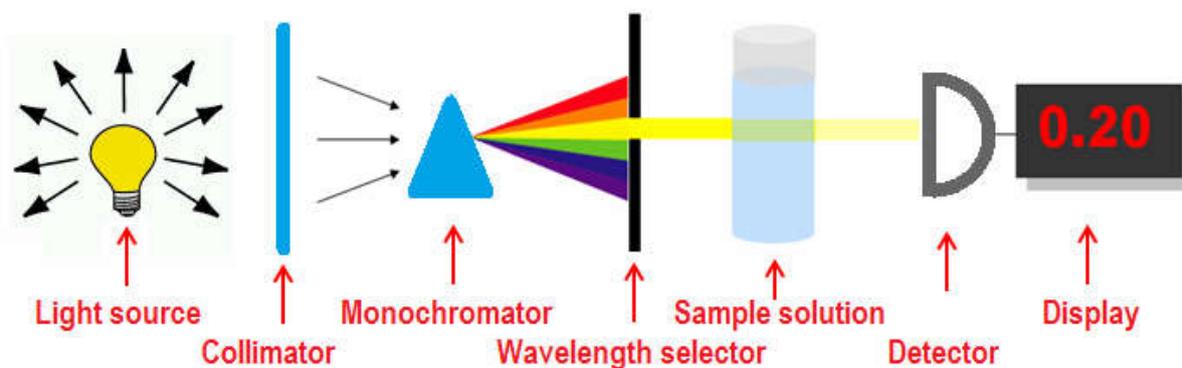
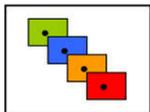


Fig. 1: Principle of UV-VIS spectrophotometer

Different compounds having dissimilar atomic and molecular interactions have characteristic absorption phenomena and absorption spectra. Concentration of every component may be found from the spectrophotometer measurements and calibration curve made using the samples of known concentration. [1]



Materials and methods

All of the experiments were performed with modelled wastewater – water solutions prepared from p.a. chemicals. The stock solutions were prepared in two concentrations – Stock solution A = 100 mg/L and Stock solution B = 10 mg/L (25 mL of stock solution A was dissolved in 250 mL distilled water in volumetric flask), the solutions for the calibration curve were prepared by dilution of these stock solutions in most cases in this manner:

Concentration C (mg/L)	100	80	60	40	20	10	9	8	7
Stock solution A V ₁ (mL)	50	40	30	20	10	5	4.5	4	3.5
Volumetric flask V ₂ (mL)	50	50	50	50	50	50	50	50	50

Concentration C (mg/L)	6	5	4	3	2	1	0.5	0.2	0.1
Stock solution B V ₁ (mL)	30	25	20	15	10	5	2.5	1	0.5
Volumetric flask V ₂ (mL)	50	50	50	50	50	50	50	50	50

Spectrophotometric determinations were realized on Spectrophotometer TermoSpectronic GENESISTM in 5 cm quartz cuvette. In the case of the higher absorbances (up to 2.500), where the dependence of absorbance on the concentration is still linear, we used the cuvette with less optical width (1 and 2 cm) and extrapolated the results to a 5 cm cuvette in the sense of Lambert-Beer's law. All of measurements were realized in triplicates. Detailed description of the used methods is reported in following session.

Chromium determination with 1,5-diphenylcarbazine

The reaction of Cr⁶⁺ with 1,5-diphenylcarbazine is very sensitive and highly selective, and therefore especially suited to the detection of very small amount of chromium. Since the chromium must be present as Cr⁶⁺ for complex formation, a prior oxidation is usually necessary. The formation of complex takes place best in acid solution (0.5 mol/L H₂SO₄).

Interferences: There is no interferences from alkali and alkaline-earth metals Ag, Al, As, Au, Bi, Cd, Ca, Hg, Mn²⁺, Ni, Pb, Pt, Sb, Sn, Ti, U, W, Zn, Mo⁶⁺ and Cu interfere from 10-fold the amount of chromium. [1, 2]

- **Reagents:**

- *diphenylcarbazine solution:* 0.25 g of 1,5-diphenylcarbazine and 4 g of phthalic anhydride are dissolved in 98 % ethanol in 100 mL volumetric flask,
- *sulphuric acid solution:* 2.78 mL of conc. 96 % H₂SO₄ is dissolved in distilled water in 100 mL volumetric flask,
- *potassium chromate solution* (Stock solution A: c(Cr⁶⁺) = 100 mg/L): 0.3735 g K₂CrO₄ is dissolved in 1000 mL distilled water in volumetric flask.

- **Procedure:**

1. to 30 mL of sample (solutions in concentration range) add 10 mL of sulphuric acid and mix it,
2. add 1 mL of diphenylcarbazine solution and adjust the volume to 50 mL with distilled water,
3. after 10 minutes the stain remains and the absorbance is measured at 540 nm against a blank prepared in the same way.

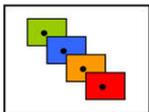
Nickel determination with dimethylglyoxime (Čugajev reagent)

Dimethylglyoxime forms with some metals (Ni, Pd²⁺, Pt²⁺, Pb and Bi) coloured complexes which are only slightly soluble in water. Nickel salts in alkali or ammoniac solutions with dimethylglyoxime (D) yield a characteristic vine red colour caused by [NiD₃]²⁻ complex.

Interferences: The method is disturbed by Pb Hg⁺, Hg²⁺, Bi, Ag, Cu, Sb, Al, Cr, Be, Fe²⁺, Fe³⁺, Mn, Ce, Sr, Mg, Zr, Pt, Th, U and Sn⁴⁺ by formation of precipitates and Co, Au³⁺, Cr⁶⁺ by their colouring. [2, 3]

- **Reagents:**

- *dimethylglyoxime solution:* 1 g of dimethylglyoxime is dissolved in 98 % ethanol in 100 mL volumetric flask,
- *ammonium persulphate solution:* 10 g of NH₄S₂O₈ is dissolved in 90 mL of distilled water,
- *ammonium hydroxide:* conc., p.a.,
- *nickel nitrate solution* (Stock solution A: c(Ni²⁺) = 100 mg/L): 0.4953 g Ni(NO₃)₂ is dissolved in 1000 mL distilled water in volumetric flask.



• **Procedure:**

1. to 3 mL of sample (solutions in concentration range) add 5 mL of ammonium persulphate solution,
2. after 10 minutes add 3 mL of conc. ammonium hydroxide, 3 mL of dimethylglyoxime solution and mix it,
3. adjust the volume to 50 mL with distilled water, after 15 minutes the stain remains and the absorbance is measured at 445 nm against a blank prepared in the same way.

Copper determination with diethyldithiocarbamate (Kupral)

Copper is one of the many elements which form complexes with sodium diethyldithiocarbamate (Na-DDTC). The yellow - brown chelate Cu(DDTC)_2 complex is formed in the pH 4 – 11. In the diluted aqueous solutions is this complex of very fine suspended, and therefore can be measured directly. The colour complex is sensitive to light, and should therefore be exposed to daylight as little as possible.

Interferences: No interferences are caused by 2 g of Cl^- , Br^- , I^- , F^- , SO_3^{2-} , SO_4^{2-} , NO_3^- , PO_4^{3-} , citrate, tartrate, oxalate, Mo^{6+} , Pb^{2+} , Zn^{2+} , less than 1 g of As^{5+} , Cd^{2+} , Sn^{2+} , W^{6+} , Al^{3+} , Ag, Co, Cr, Fe, Hg, Mn, Ni, V interfere. [2, 3]

• **Reagents:**

- *diethyldithiocarbamate solution:* 1 g of sodium diethyldithiocarbamate is dissolved in redistilled water in 100 mL volumetric flask,
- *ammonium hydroxide:* conc., p.a.,
- *copper chloride solution* (Stock solution A: $c(\text{Cu}^{2+}) = 100 \text{ mg/L}$): 0.3533 g $\text{CuCl}_2 \cdot 5\text{H}_2\text{O}$ is dissolved in 1000 mL distilled water in volumetric flask.

• **Procedure:**

1. to 50 mL of sample (solutions in concentration range) add 1 mL of conc. ammonium hydroxide, 1 mL of diethyldithiocarbamate solution and mix it,
2. after 15 minutes the stain remains and the absorbance is measured at 447 nm against a blank prepared in the same way.

Copper determination with ammonia

Determination of copper based on intense coloured tetra ammine complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is less accurate and sensitive determination than others, but it is quick and easy. The blue colour is measured at 620 nm.

Interferences: Determination interfere elements providing with NH_4OH coloured complexes (Co, Ni), anions bound to Cu (tartrates, citrates, cyanides), Mn^{6+} , Cr^{6+} , SiO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$. Determination don't interfere Ag, Cd, Zn a Pd. [2, 3]

• **Reagents:**

- *ammonium hydroxide:* conc., p.a.,
- *copper chloride solution* (Stock solution A: $c(\text{Cu}^{2+}) = 100 \text{ mg/L}$): 0.3533 g $\text{CuCl}_2 \cdot 5\text{H}_2\text{O}$ is dried in desiccator and dissolved in 1000 mL distilled water in volumetric flask.

• **Procedure:**

1. to 50 mL of sample (solutions in concentration range) add 1 mL of conc. ammonium hydroxide and mix it,
2. after 15 minutes the stain remains and the absorbance is measured at 620 nm against a blank prepared in the same way.

Cobalt determination with thiocyanate

Co^{2+} ions give with thiocyanate the blue coloured cobalt thiocyanate complex. At a low concentration of the SCN^- is light coloured, and is attributed to the complex cations $[\text{Co}(\text{SCN})]^{+}$. The excess is again intense and corresponds to the anion $[\text{Co}(\text{SCN})_4]^{2-}$. The spectrophotometric measurement of the blue complex is realized in an aqueous medium in the presence of ethanol or acetone, which increasing complex formation by decreasing the dielectric constant of the solution.

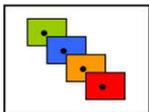
Interferences: The method is disturbed by Ni, Cr, Mn, Ti, U and Mo, which provide the same conditions discoloration. Ca, Sr, Ba, W, Ag and Hg^+ form a precipitate. Hg^{2+} consumes the agent to form little dissociated $\text{Hg}(\text{SCN})_2$. In the solution must not be present CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ a Ce^{4+} . Other elements, if not a greater than 100-fold excess do not interfere with the determination. [2, 3]

• **Reagents:**

- *hydrochloric acid solution:* 25 mL of conc. 36 % HCl is dissolved in 25 mL of distilled water,
- *ammonium thiocyanate solution:* 30 g of NH_4SCN is dissolved in 20 mL of distilled water,
- *acetone:* conc., p.a.,
- *cobalt chloride solution* (Stock solution A: $c(\text{Co}^{2+}) = 100 \text{ mg/L}$) 0.4043 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ is dissolved in 1000 mL distilled water in volumetric flask.

• **Procedure:**

1. to 10 mL of sample (solutions in concentration range) add 1 mL of hydrochloric acid solution, 0.5 mL of NH_4SCN and mix it,
2. add 20 mL of acetone,



3. after 10 minutes the stain remains and the absorbance is measured at 625 nm against a blank prepared in the same way.

Aluminium determination with aurin tricarboxylic acid ammonium salt (Aluminon)

Aurin tricarboxylic acid ammonium salt forms brilliantly coloured lakes with a number of metal ions. The intensively red coloured lake with aluminium is utilized for detection and determination of this metal ion. The formation and stability of the lake depend on the pH value is 5.3 in acetate buffered solution, and the greatest intensity of colour is attained after 15 minutes at room temperature. Gelatines, gum Arabic or starch are used as protective colloid to stabilize the colour. [4]

Interferences: Aurin tricarboxylic acid ammonium salt is not particularly selective. The following ions can interfere in the determination of aluminium: Ba, Be, Ca, Ce, Cr, Er, Fe, Ga, Hf, In, La, Mg, Na, Sc, Sr, Th, Zr. The interferences can, however, largely be excluded if the lake formed in treated with ammoniacal or ammonium carbonate solution. The colour lakes of Al, Be and Cr persist, while others are decoloured. Interference by Fe^{3+} may be excluded by addition of thioglycol or thioglycolic acid. [2, 3]

• **Reagents:**

- *aluminone solution:* 25 g of $\text{CH}_3\text{COONH}_4$ is dissolved in 100 mL redistilled water, carefully are added 31.5 mL conc. HCl, then the solution of aluminone (0.225 g of Aurin tricarboxylic acid ammonium salt is dissolved in 50 mL redistilled water) and 2.5 g of gelatine. The solution is filtered and dissolved in 250 mL distilled water in volumetric flask.
- *thioglycol solution:* 1 mL of thioglycol is dissolved in redistilled water in 100 mL volumetric flask,
- *aluminium nitrate solution* (Stock solution A: $c(\text{Al}^{3+}) = 100 \text{ mg/L}$): 1.3908 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is dissolved in 1000 mL distilled water in volumetric flask.

• **Procedure:**

1. to 5 mL of sample (solutions in concentration range) add 0.5 mL of thioglycol solution, 5 mL of aluminone solution and mix it,
2. adjust the volume to 50 mL with distilled water,
3. take to heavy walled tube the volume of sample required for spectrophotometric analysis and a heating it in a water bath for 20 minutes,
4. after cooling to room temperature the absorbance is measured at 530 nm against a blank prepared in the same way.

Arsenic determination as molybdenum blue

Molybdenum blue method is one of the most sensitive methods for the photometric determination of As. As^{5+} as AsO_4^{3-} react with MoO_4^{2-} in a 0.5 – 1 mol/L H_2SO_4 like as PO_4^{3-} to form complex molybdenoarsenic acid, which is subsequently reduced to molybdenum blue. The reduction is commonly realized by hydrazine sulphate, ascorbic acid and it is also possible to use SnCl_2 . The resulting blue (700 nm) is slowly changed over 24 hours at steady tone (840 nm), while hydrazine sulphate provides the intense blue almost immediately.

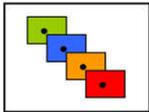
Interferences: Determination interfere P, Si, Ge, which providing the same reaction, Fe^{2+} , S^{2-} , $\text{S}_2\text{O}_3^{2-}$, a SCN^- reduce in the solution present MoO_4^{2-} , Ba, Sr a Pb is in the particular solution reduced as sulphates. [2, 3]

• **Reagents:**

- *sulphuric acid solution* ($c = 2.5 \text{ mol/L}$): 140 mL of H_2SO_4 concentrate is dissoluble in 2000 mL flask bank in 800 mL of distilled water, prepare solution on ice to chill, adjust the volume to 2000 mL with distilled water,
- *ammonium molybdate solution:* 15 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ is dissoluble in 500 mL volume flask in distilled water,
- *potassium antimonyl tartrate solution:* 0.68 g of $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 1/2\text{H}_2\text{O}$ is dissoluble in distilled water in 500 mL volumetric flask,
- *ascorbic acid solution:* 2.16 g of ascorbic acid is dissoluble in distilled water in 100 mL volumetric flask,
- *mixed agent:* is prepared only in the required amount before use. It is a mixed of 125 mL of H_2SO_4 solution, 50 mL of ammonium molybdate solution, 25 mL of potassium antimonyl tartrate solution and 50 mL of ascorbic acid solution. Reagent is stable for about 4 hours.
- *sodium hydrogen arsenate solution* (Stock solution A: $c(\text{As}^{5+}) = 100 \text{ mg/L}$): 0.4279 g $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ is dissolved in 1000 mL distilled water in volumetric flask.

• **Procedure:**

1. to 50 ml of the sample (or solution in concentration range supplemented distilled water 50 ml) was added to 100 mL Erlenmeyer flask,
2. add 5 mL of mixed agent and mixed,
3. after 30 minutes the stain remains and the absorbance is measured at 600 nm against a blank prepared in the same way.



Iron determination with thiocyanate

Fe^{3+} reacts in an acidic medium with SCN^- ions to form red coloured complex $[\text{Fe}(\text{SCN})]^{2+}$. In aqueous solutions is colour of complex not stable, it is influenced by the concentration of thiocyanate, pH, ionic strength of the solution, duration, complex is sensitive to light. Addition of oxidizing agents, such as sodium persulphate or hydrogen peroxide increases the colour stability, because the trivalent iron is not reduced in the light of the thiocyanate. [1]

Interferences: Interferences which can be caused by Bi, Co, Cu, Mo, Ti, Nb, U, Ru, Ir, Os, Hg^{2+} , Cd, Zn, Sb^{3+} , F^- , PO_4^{3-} . Hg^+ and Ag salts produce the turbidity. In presence of higher concentrations of Ni and Co we can measured in the presence of citric acid. [2, 3]

• **Reagents:**

- *sulphuric acid solution:* 12.5 mL of conc. 96 % H_2SO_4 is dissolved in 25 mL of distilled water,
- *hydrochloric acid solution:* 25 mL of conc. 36 % HCl is dissolved in 25 mL of distilled water,
- *potassium thiocyanate solution:* 10 g of KSCN is dissolved in 40 mL of distilled water,
- *potassium permanganate solution:* 0.32 g of KMnO_4 is dissolved in water in 100 mL volumetric flask,
- *oxalic acid solution:* 0.63 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ is dissolved in water in 100 mL volumetric flask,
- *ammonium iron sulphate solution* (Stock solution A: $c(\text{Fe}^{2+}) = 100 \text{ mg/L}$): 0.8634 g $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is dissolved in 1000 mL distilled water in volumetric flask.

• **Procedure:**

1. the 50 mL of sample (solutions in concentration range) pipetted into a boiling flask,
2. add 2.5 mL of H_2SO_4 and 2.5 mL of KMnO_4 , the mixture was boiled for 3 – 5 minutes to evaporate at least 5 mL of the mixture,
3. still hot solution decolorize with oxalic acid and re-stained with a few drops of KMnO_4 to a pink (if it becomes cloudy, carefully re-colourless it),
4. the volume is adjusted to 50 mL and add 2.5 mL HCl and 5 mL of thiocyanate solution,
5. after 10 minutes the stain remains and the absorbance is measured at 500 nm against a blank prepared in the same way.

Manganese determination with formaldoxime

Formaldoxime in alkaline medium with manganese ions forms a water soluble orange-red colour complex $(\text{CH}_2\text{NO})_3\text{Mn}$ in which the manganese is trivalent. Bivalent manganese is similarly capable of reacting, but is oxidized by atmospheric oxygen in complex to trivalent manganese. Formation of colour takes place within a few minutes and the colour is stable for 16 hours. An excess of ammonia used to make solution alkaline does not have any adverse effect. The absorbance is measured at 450 nm.

Interferences: Interferences which can be caused by iron and copper may be eliminated by masking with cyanide in the present of tartrate and subsequent removal of excess of cyanide with zinc sulfate solution. Vanadium and Uranium interfere, and the elements Bi, Hg and Ti give rise to turbidities in alkaline solutions. [2, 3]

• **Reagents:**

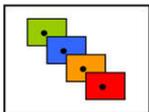
- *tetrasodium ethylenediaminetetraacetate solution* (Na_4EDTA , chelation 3): 10 g of Na_4EDTA is dissolved in water in 100 mL volumetric flask,
- *formaldoxime:* 10 g of hydroxylamine is dissolved in 50 mL of distilled water, add 5 mL of conc. 35 % formaldehyde and adjust the volume to 100 mL with distilled water. The solution must be prepared fresh daily,
- *ferrous ammonium sulphate solution:* 0.7 g of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ is dissolved in 500 mL of distilled water, add 0.2 mL of conc. 96 % sulphuric acid and adjust the volume to 1000 mL with distilled water,
- *sodium hydroxide solution:* 16 g of NaOH is dissolved in water, after cooling to room temperature, adjust the volume to 100 mL with distilled water,
- *manganese chloride solution* (Stock solution A: $c(\text{Mn}^{2+}) = 100 \text{ mg/L}$): 0.3602 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ is dissolved in 1000 mL distilled water in volumetric flask.

• **Procedure:**

1. to 10 mL of sample (solutions in concentration range) add 1 mL of ferrous ammonium sulphate solution, 2 mL of Na_4EDTA and mix it,
2. add 1 mL of formaldoxime and immediately 2 mL of NaOH,
3. adjust the volume to 50 mL with distilled water, after 10 minutes the stain remains and the absorbance is measured at 450 nm against a blank prepared in the same way.

Magnesium determination with eriochrome black

In alkaline solution (~ 10) Eriochrome black T forms with magnesium ions a red, water-soluble complex. At $\text{pH}=10.6$ the absorption maximum of the colour complex is at 560 nm. The colour is not stable, but persists for 30 minutes. On



adherence to certain conditions, such as pH value and buffering, a satisfactory reproducibility of the method may be attained.

Interferences: Al, Ca, Co, Cu, Fe, Mn, Ni a Zn interfere. Ca does not yet interfere in ratio Ca:Mg = 1:1, and Fe similarly does not interfere until in 10-fold excess. Na and K interfere at a concentration greater than 0.01 mol/L as the result of salt effect. [2, 3]

• **Reagents:**

- *eriochrome black T solution:* 0.1 g of 2-Hydroxy-1-(1-hydroxy-2-naphtylazo)-6-nitroinaphthalene-4-sulfonic acid sodium salt is dissolved in 100 mL of methanol and 10 mL of this solution is diluted with methanol in 100 mL volumetric flask. The solution must be prepared fresh daily.
- *buffer solution:* dissolve 1 g ammonium chloride in a mixture of 50 mL 25 % ammonia solution and 50 mL water.
- *magnesium sulphate solution* (Stock solution A: $c(\text{Mg}^{2+}) = 100 \text{ mg/L}$): 0.4953 g MgSO_4 is dissolved in 1000 mL distilled water in volumetric flask,

• **Procedure:**

1. to 10 mL of nearly natural sample (solutions in concentration range) add 2.5 mL of buffer solution and 5 mL of Eriochrome black T solution and mix it,
2. adjust the volume to 50 mL with distilled water,
3. the absorbance is measured at 530 nm against a blank prepared in the same way.

Calcium determination with murexide

Murexide (ammonium salt of purple acid) forms with ions Ca^{2+} red coloured chelate, whose colour intensity increases with increasing alkalinity. At pH 11.3, when it is biggest difference between absorbance of complex and absorbance of reagent, the colour reaction is about 20 times more sensitive than at pH 6. At the expense of increasing the sensitivity decrease the stability of a coloured complex, at pH > 12 there is quite a considerably rapid red colour decomposition.

Interferences: The determination does not interfere in the alkaline pH, roughly the same range of Mg, Ba, significant excess Na, K a Cs, Pb, Be, Al, Cr, Ti^{4+} , As, NH_4^+ . From interfering metals Cu, Hg^{2+} , Ag, Co, Cd, Zn, Ni, Mg the major part can be fixed with KCN. [2, 3]

• **Reagents:**

- *murexide solution:* 0.04 g of ammonium 2,6-dioxo-5-[(2,4,6-trioxo-5-hexahydropyrimidinylidene)amino]-3H-pyrimidin-4-olate is dissolved in 75 mL distilled water and supplement by ethanol to volume 250 mL. The solution must be prepared fresh daily.
- *sodium hydroxide solution:* 0,4 g of NaOH is dissolved in water, after cooling to room temperature, adjust the volume to 100 mL with distilled water,
- *calcium nitrate solution* (Stock solution A: $c(\text{Ca}^{2+}) = 100 \text{ mg/L}$): 0.5893 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is dissolved in 1000 mL distilled water in volumetric flask.

• **Procedure:**

- to 10 mL of sample (solutions in concentration range) add 2 mL of NaOH,
- adjust the volume to 50 mL with distilled water,
- after 10 minutes the stain remains and the absorbance is measured at 505 nm against a blank prepared in the same way.

Strontium determination with murexide

Murexide reacts sensitively with Sr to form intensely red coloured chelate. The determination is carried out at pH 11.3.

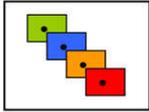
Interferences: The determination many metals interfere, e.g. Mg, Ca, Ba, Li, K, and Ag, and therefore they must be pre-separated. [2, 3]

• **Reagents:**

- *murexide solution:* 0.125 g of ammonium 2,6-dioxo-5-[(2,4,6-trioxo-5-hexahydropyrimidinylidene)amino]-3H-pyrimidin-4-olate is dissolved in 45 mL distilled water and 200 ml of anhydrous ethylene glycol. The solution must be prepared fresh daily.
- *sodium hydroxide solution:* 0.4 g of NaOH is dissolved in water, after cooling to room temperature, adjust the volume to 100 mL with distilled water,
- *ethylene glycol anhydrous:* conc., p.a.,
- *strontium chloride solution* (Stock solution A: $c(\text{Sr}^{2+}) = 100 \text{ mg/L}$): 0.3043 g of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ is dissolved in 1000 mL distilled water in volumetric flask.

• **Procedure:**

1. 10 mL of sample (solutions in concentration range) is evaporated in an dish,
2. after cooling down, add few mL of water and quantitatively transferred it to a 50 mL volumetric flask,
3. add 30 mL of ethylene glycol, 3 mL NaOH and adjust the volume to approximately 40 mL with distilled water,



4. add 6 mL of murexide solution and adjust the volume to 50 mL with distilled water,
5. after 10 minutes the stain remains and the absorbance is measured at 530 nm against a blank prepared in the same way.

Results and discussion

Chromium

Chromium is a lithophile metallic element, which naturally occurs in the oxidation state Cr^{2+} , but mainly Cr^{3+} and Cr^{6+} . Chromium is used largely to make steel alloys, dyes and chemicals. Major man-made sources of environmental pollution comprise industrial wastewaters, mainly from galvanizing plants, textile and leather industries. [5]

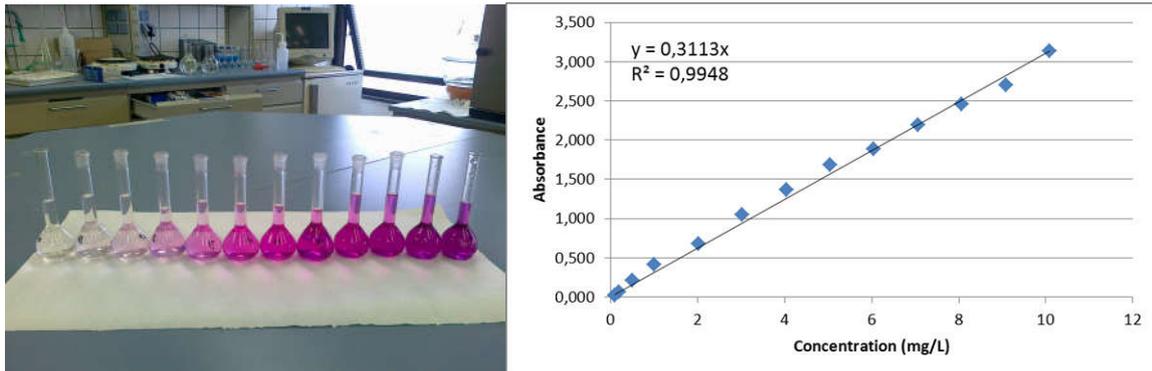


Fig. 2: The colour of Cr-complex and calibration curve for spectrophotometric determination

Calibration curve was reported as linear between 0 – 10 mg/L ($A = 0 - 3.140$) in the form:

$$A = 0.3113 \times c \quad R^2 = 0.9948$$

where A is absorbance and c is concentration of element in mg/L. For n millilitres taken to analyse, concentration can be calculated from equation:

$$c = \frac{30}{n} \times \frac{A}{0.3113}$$

Nickel

Nickel is a metallic element with siderophile, chalcophile and lithophile properties which occurs in nature in oxidation states Ni^{1+} , Ni^{3+} , but mainly Ni^{2+} . Nickel is used mainly in the steel industry, a considerable percentage being recycled. Environmental impacts are caused largely by industrial dust, wastes and wastewaters. [5]

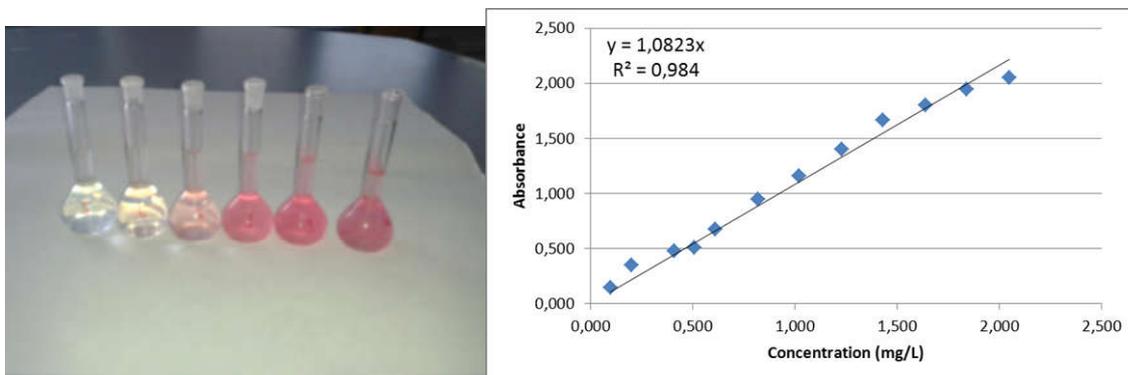
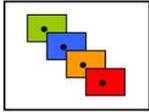


Fig. 3: The colour of Ni-complex and calibration curve for spectrophotometric determination

Calibration curve was reported as linear between 0 – 2 mg/L ($A = 0 - 2.049$) in the form:

$$A = 1.0823 \times c \quad R^2 = 0.9840$$



where A is absorbance and c is concentration of element in mg/L. For n millilitres taken to analyse, concentration can be calculated from equation:

$$c = \frac{3}{n} \times \frac{A}{1.0823}$$

Copper

Copper is a chalcophile element which occurs in nature in the oxidation states Cu^0 , Cu^{1+} , but mainly Cu^{2+} . Copper is a base metal widely used primarily in the smelting, electro – engineering and chemical industries. Man – made copper contamination occurs largely in the vicinity of smelting plants, fungicide spraying in agriculture, vineyards, etc. [5]

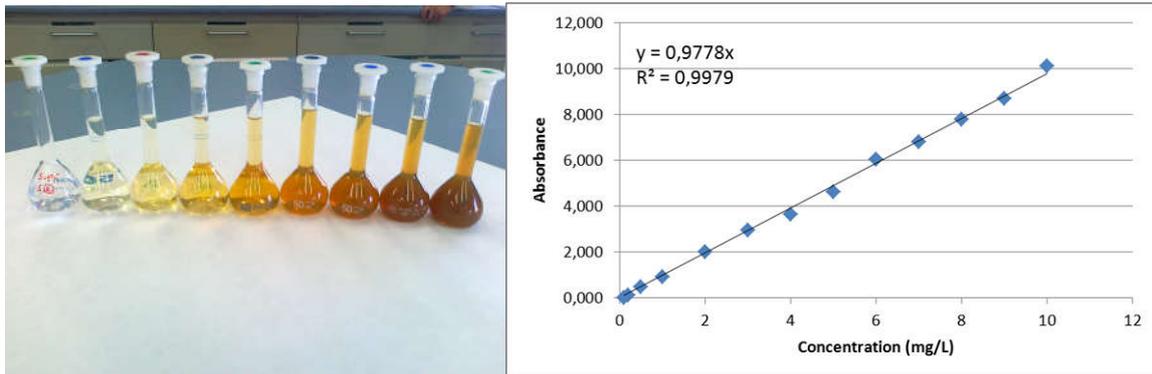


Fig. 4: The colour of Cu-complex and calibration curve for spectrophotometric determination

Calibration curve was reported as linear between 0 – 10 mg/L ($A = 0 - 10.085$) in the form:

$$A = 0.9878 \times c \quad R^2 = 0.9979$$

where A is absorbance and c is concentration of element in mg/L. For n millilitres taken to analyse, concentration can be calculated from equation:

$$c = \frac{50}{n} \times \frac{A}{0.9878}$$

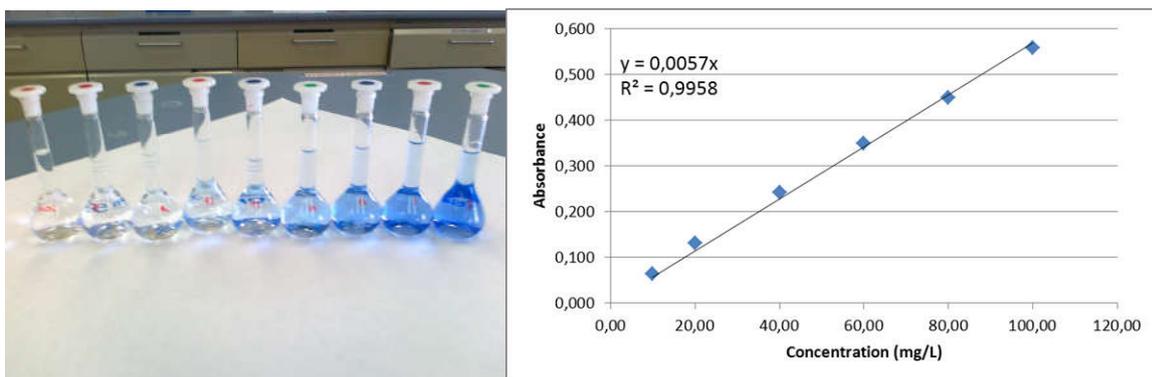
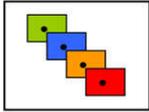


Fig. 5: The colour of Cu-complex and calibration curve for spectrophotometric determination

For high concentration is useful to use simple reaction of copper ions with ammonia solution. Calibration curve was reported as linear between 10 – 100 mg/L ($A = 0.064 - 0.558$) in the form:

$$A = 0.0057 \times c \quad R^2 = 0.9958$$

where A is absorbance and c is concentration of element in mg/L. For n millilitres taken to analyse, concentration can be calculated from equation:



$$c = \frac{50}{n} \times \frac{A}{0.0057}$$

Cobalt

Cobalt is metallic element naturally occurring in the oxidation states Co^{2+} and Co^{3+} . It has both lithophile and chalcophile properties similar to nickel. Cobalt is used in steel – making, the majority of it being recycled. Its word production is not very high and therefore it is not regarded as an element with a major man – made impact on environment, except in the vicinity of smelting plants. [5]

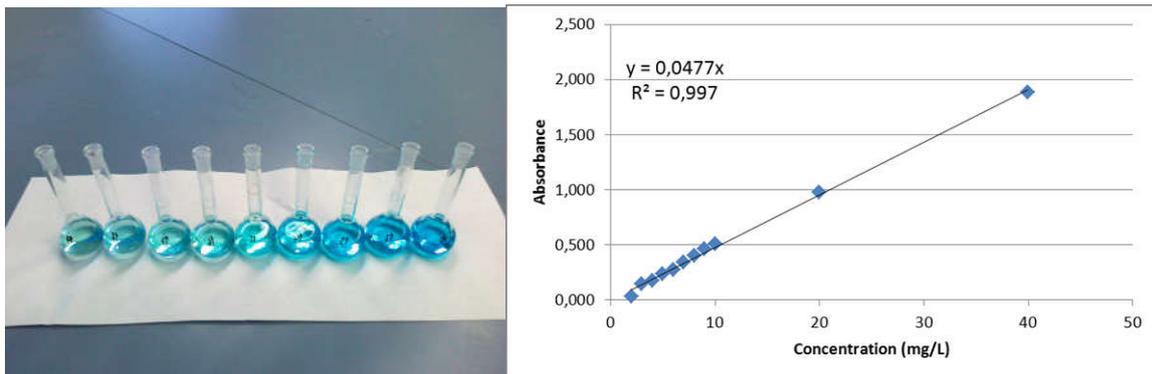


Fig. 6: The colour of Co-complex and calibration curve for spectrophotometric determination

Calibration curve was reported as linear between 0 – 40 mg/L ($A = 0 - 1.881$) in the form:

$$A = 0.0477 \times c \quad R^2 = 0.9970$$

where A is absorbance and c is concentration of element in mg/L. For n millilitres taken to analyse, concentration can be calculated from equation:

$$c = \frac{10}{n} \times \frac{A}{0.0477}$$

Aluminium

Aluminium is a major metallic lithophile element naturally occurring in the oxidation state Al^{3+} . From an economic point of view, aluminium ranks among the most important light metals. It is released into the environment as industrial wastes. Because of its high natural content it is extremely difficult to determine the share of man – made contamination. [5]

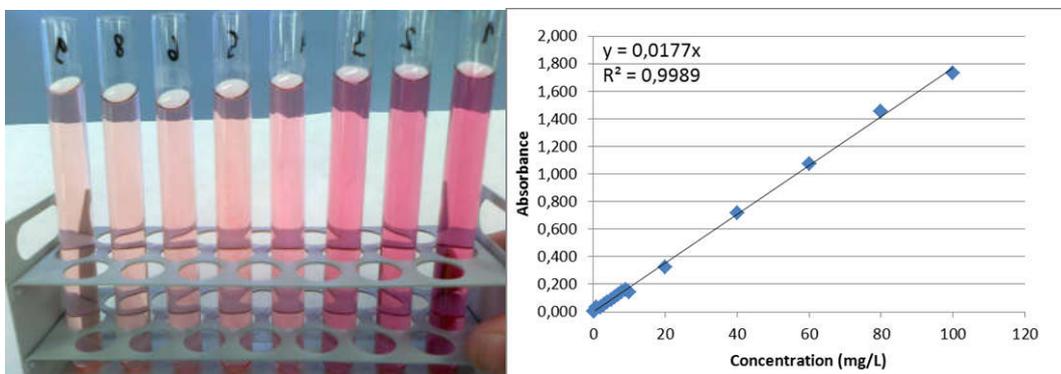
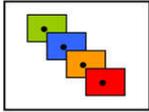


Fig. 7: The colour of Al-complex and calibration curve for spectrophotometric determination

Calibration curve was reported as linear between 0 – 100 mg/L ($A = 0 - 1.735$) in the form:



$$A = 0.0177 \times c \quad R^2 = 0.9989$$

where A is absorbance and c is concentration of element in mg/L. For n millilitres taken to analyse, concentration can be calculated from equation:

$$c = \frac{5}{n} \times \frac{A}{0.0177}$$

Arsenic

Arsenic occurs naturally in oxidation states As^{3-} , As^0 , As^{3+} and As^{5+} , the latter being the most widespread. Arsenic is produced as by – product of the processing of polymetallic sulphides. Major man – made sources of contamination are chiefly mining, smelting, power generation in thermal power plants and pesticides. [5]

Calibration curve was reported as linear between 0 – 20 mg/L ($A = 0 – 1.168$) in the form:

$$A = 0.0590 \times c \quad R^2 = 0.9926$$

where A is absorbance and c is concentration of element in mg/L. For n millilitres taken to analyse, concentration can be calculated from equation:

$$c = \frac{50}{n} \times \frac{A}{0.0590}$$

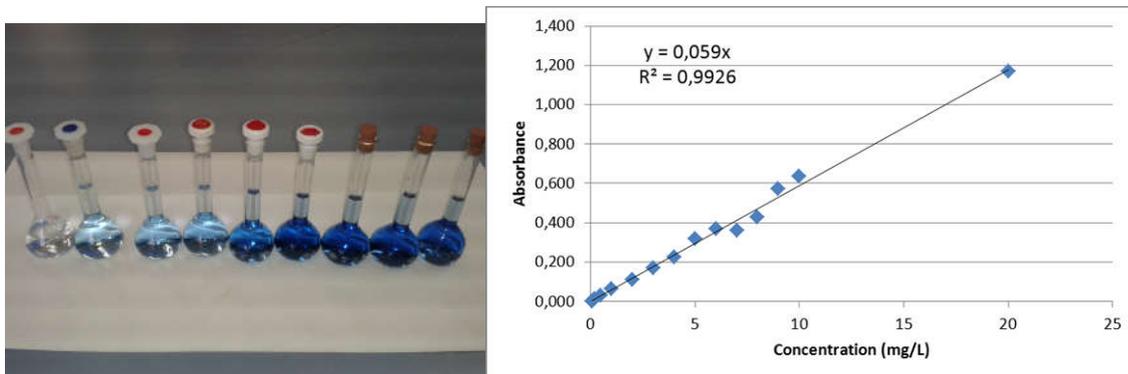
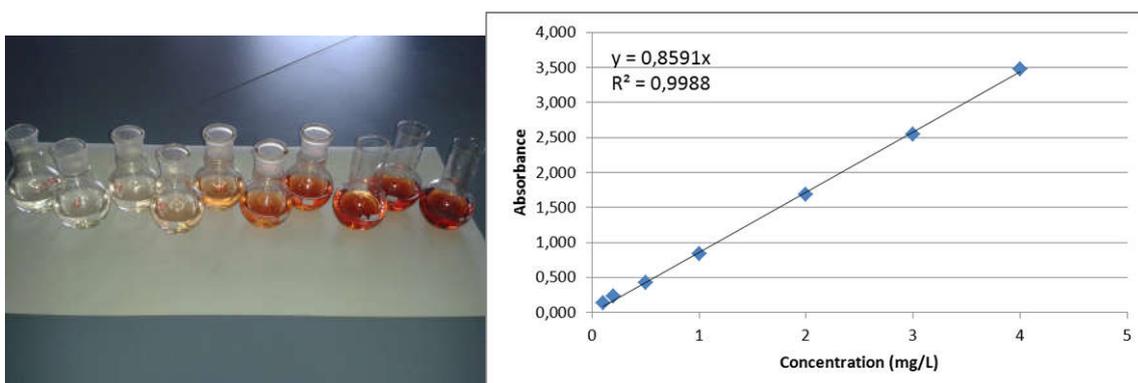


Fig. 8: The colour of As-complex and calibration curve for spectrophotometric determination

Iron

Iron is a metallic element naturally occurring in the oxidation states Fe^{2+} and Fe^{3+} . Iron is one of most widely used metals, primarily in smelting and steel industry. The amount of iron dispersed in the environment by mans large but difficult to estimate in more detail. [5]



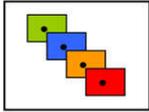


Fig. 9: The colour of Fe-complex and calibration curve for spectrophotometric determination

Calibration curve was reported as linear between 0 – 4 mg/L ($A = 0 - 3.480$) in the form:

$$A = 0.8591 \times c \quad R^2 = 0.9988$$

where A is absorbance and c is concentration of element in mg/L. For n millilitres taken to analyse, concentration can be calculated from equation:

$$c = \frac{50}{n} \times \frac{A}{0.8591}$$

Manganese

Manganese is a metallic, lithophile trace element naturally occurring in the oxidation states Mn^{3+} , Mn^{5+} , Mn^{6+} , Mn^{7+} , but mainly Mn^{2+} and Mn^{4+} . Manganese is used primarily in the smelting and chemical industries. Its man – made dispersal into the environment is on minor importance. [5]

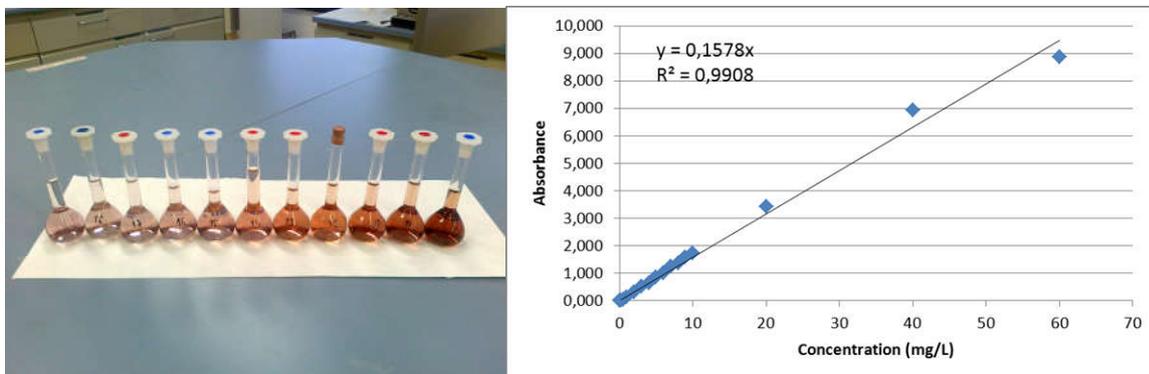


Fig. 10: The colour of Mn-complex and calibration curve for spectrophotometric determination

Calibration curve was reported as linear between 0 – 60 mg/L ($A = 0 - 8.870$) in the form:

$$A = 0.1578 \times c \quad R^2 = 0.9905$$

where A is absorbance and c is concentration of element in mg/L. For n millilitres taken to analyse, concentration can be calculated from equation:

$$c = \frac{10}{n} \times \frac{A}{0.1578}$$

Magnesium

Magnesium is one of major lithophile elements and, like the other alkali – earth metals (Be, Ca, Sr, Ba), is found in nature in the oxidation state Mg^{2+} . Magnesium is used as a light metal, but in quantities insignificant compared to other applications, such as refractory (magnesite) or a constituent of cement. Man – made magnesium contaminates environment in the form of fertilizers and wastes of various kinds which strongly disturb its natural distribution. [5]

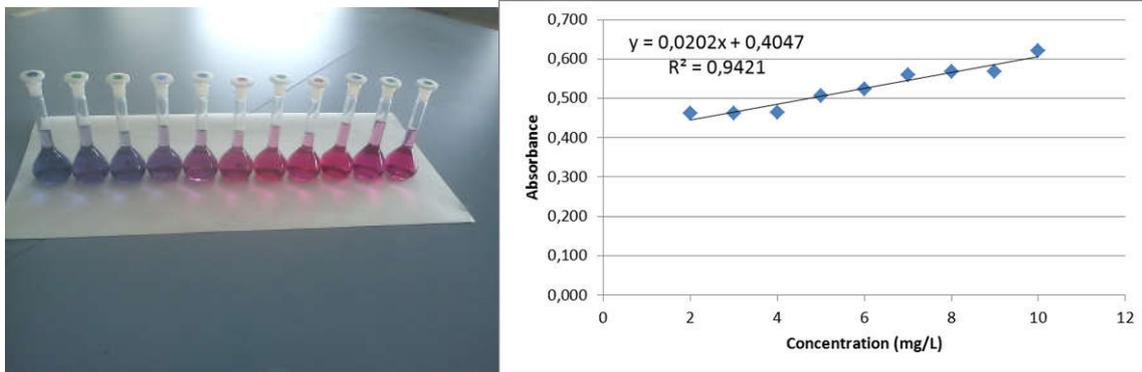
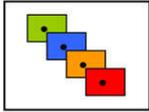


Fig. 11: The colour of Mg-complex and calibration curve for spectrophotometric determination

Calibration curve was reported as linear between 2 – 10 mg/L ($A = 0.0462 - 0.621$) in the form:

$$A = 0.0202 \times c + 0.4047 \quad R^2 = 0.9421$$

where A is absorbance and c is concentration of element in mg/L. For n millilitres taken to analyse, concentration can be calculated from equation:

$$c = \frac{10}{n} \times \frac{A - 0.4047}{0.0202}$$

Calcium

Calcium is an alkali-earth metal naturally occurring in the oxidation state Ca^{2+} . It is widely used as building materials, fertilizers, in chemical industry, etc. Its man – made distribution does not essentially affect the environment, the only exception being cement plants. [5]

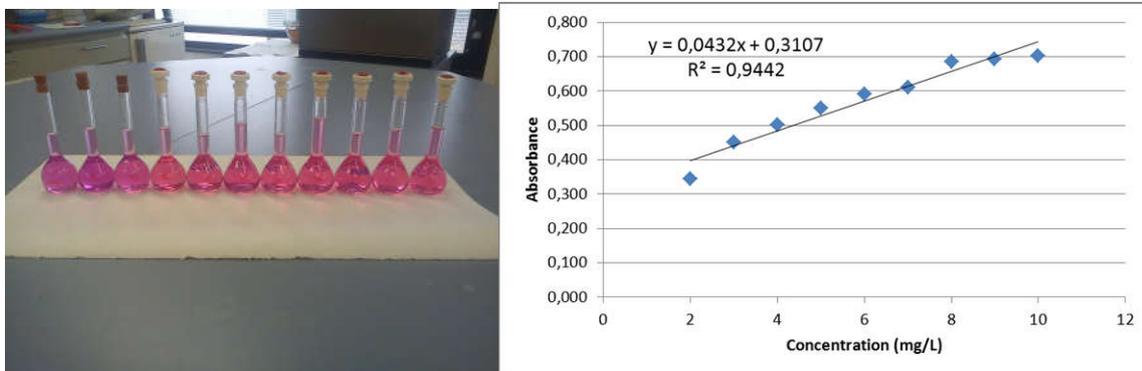


Fig. 12: The colour of Ca-complex and calibration curve for spectrophotometric determination

Calibration curve was reported as linear between 2 – 10 mg/L ($A = 0.344 - 0.703$) in the form:

$$A = 0.0432 \times c + 0.3107 \quad R^2 = 0.9442$$

where A is absorbance and c is concentration of element in mg/L. For n millilitres taken to analyse, concentration can be calculated from equation:

$$c = \frac{10}{n} \times \frac{A - 0.3107}{0.0432}$$

Strontium

Strontium is lithophile element. In nature it is found in the oxidation state Sr^{2+} . The world strontium output is fairly low, and so are its technological importance, commercial consumption and man – made contamination. Strontium radionuclides produced in nuclear power plants and nuclear weapons, however, pose an environmental threat. [5]

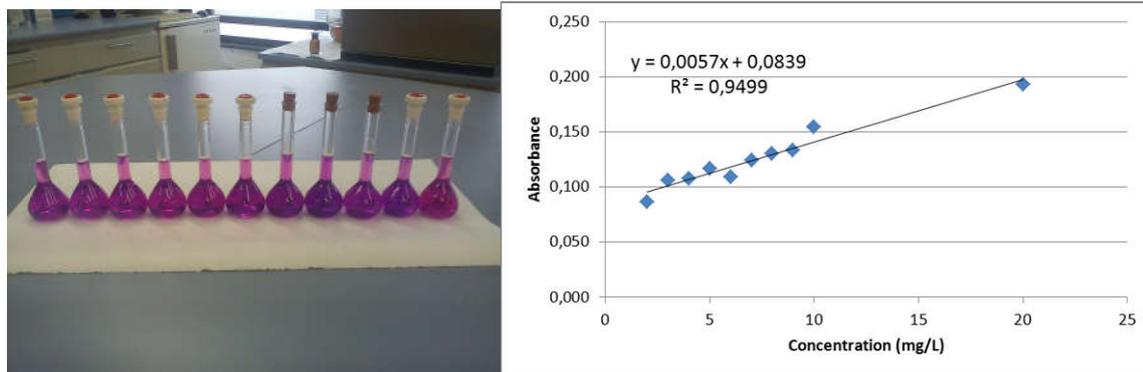
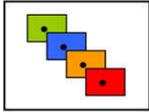


Fig. 13: The colour of Sr-complex and calibration curve for spectrophotometric determination

Calibration curve was reported as linear between 2 – 20 mg/L ($A = 0.086 - 0.193$) in the form:

$$A = 0.0057 \times c + 0.0839 \quad R^2 = 0.9499$$

where A is absorbance and c is concentration of element in mg/L. For n millilitres taken to analyse, concentration can be calculated from equation:

$$c = \frac{10}{n} \times \frac{A - 0.0839}{0.1578}$$

Conclusions

Methods of UV – VIS spectrophotometry for reported elements determination is beside modern analytical methods often considered as ancient. On the other hand, because of their undemanding and favourable cost, they are adequate for simulation a many of geochemical or technological processes. They are also suitable for laboratory teaching in the bachelor and diploma theses. Many of them are, however, in the “user friendly sets” form (portable equipment with same chemical applied on strips, powders or placed in the dropped bottles) successfully used for simple terrain determinations.

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