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Bachelor's Thesis

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Studijní obor: **Konstrukce pozemních staveb**

II. ÚDAJE K BAKALÁŘSKÉ PRÁCI

Název bakalářské práce:

Využití UV/VIS spektrofotometrie pro stanovení koncentrace solí vyluhovatelných ze stavebních materiálů.

Název bakalářské práce anglicky:

Utilization of UV/VIS spectrophotometry to determine the concentration of salts leachable from building materials.

Pokyny pro vypracování:

Pro stanovení amonných iontů, dusičnanů, dusitanů, chloridů a síranů UV/VIS spektrofotometrií vypracujte kalibrační křivky jednotlivých iontů. Proveďte analýzu vybraných iontů ve vyluzích zasolených omítek

Seznam doporučené literatury:

ČSN ISO 15923-1 Kvalita vod - Stanovení vybraných ukazatelů diskretními analytickými metodami - Část 1: Amonné ionty, dusičnany, dusitany, chloridy, orthofosforečnany, sírany a křemičitany s fotometrickou detekcí, 2017.

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III. PŘEVZETÍ ZADÁNÍ

Studentka bere na vědomí, že je povinna vypracovat bakalářskou práci samostatně, bez cizí pomoci, s výjimkou poskytnutých konzultací. Seznam použité literatury, jiných pramenů a jmen konzultantů je třeba uvést v bakalářské práci.

Datum převzetí zadání

Podpis studentky

I declare that I worked on this thesis on my own under the professional supervision of Ing. Martina Záleská, Ph.D. and that I used only sources mentioned in the References section.

.....

signature

I would like to express my gratitude to my chief supervisor Ing. Martina Záleská, Ph.D., who guided me throughout this process. I am also grateful to prof. Ing. Milena Pavlíková, Ph.D., for providing me with all the necessary facilities for the research and Ing. Adam Pivák, for his valuable advice.

Utilization of UV/VIS spectrophotometry
to determine the concentration of salts
leachable from building materials

Využití UV/VIS spektrofotometrie pro
stanovení koncentrace solí vyluhovatelných
ze stavebních materiálů

Abstract:

This bachelor's thesis deals with the use of UV/VIS spectrophotometry to determine the concentration of salts in renders. The spectrophotometry is widely used analytical method. Theoretical part is focused on its principle, instrumentation and utilization. Furthermore, it defines renders, especially renovation renders and what is caused by salts presence in building materials. The experimental part includes the analysis of eluates from lime-based renders in terms of the content of selected ions - specifically ammonium, nitrates, nitrites, chlorides and sulfates. The analysis proved high concentration of some measured ions. Gained results will make for practical evaluation of utilization this method to determine the concentration of salts leachable from building materials.

Keywords: *UV/VIS spectrophotometry, optical methods, salt concentration, building materials, renovation renders*

Anotace:

Tato bakalářská práce pojednává o využití UV/VIS spektrofotometrie ke stanovení koncentrace solí v omítkách. Spektrofotometrie je analytická metoda hojně využívaná v mnoha odvětvích. Teoretická část se zaměřuje na její princip, instrumentaci a využití. Dále na definování omítek, zejména sanačních a na problémy, které způsobují soli ve stavebních materiálech. Experimentální část zahrnuje analýzu vzorků vápenných omítek z hlediska obsahu vybraných iontů – konkrétně amonných iontů, dusičnanů, dusitanů, chloridů a síranů. Laboratorní analýza prokázala vysokou koncentraci některých měřených iontů. Získaná data mají posloužit k vyhodnocení praktického využití této analytické metody při stanovování koncentrací solí vyluhovatelných ze stavebních materiálů.

Klíčová slova: *UV/VIS spektrofotometrie, optické metody, koncentrace solí, stavební materiály, sanační omítky*

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List of abbreviations and symbols

UV	ultraviolet radiation
VIS	visible radiation
IR	infrared radiation
NMR	nuclear magnetic resonance
rpm	revolutions per minute
DIC	sodium dichloroisocyanurate
NED	N-(1-naphthyl)ethylenediamine dihydrochloride
f, ν [Hz]	frequency
λ [m]	wavelength
ϕ [W]	radiant flux
I [W/m^2]	irradiance
T [-]	transmittance
A [-]	absorbance
ε [$\text{dm}^3/(\text{mol}\cdot\text{cm})$]	molar absorption coefficient
c [mol/dm^3]	molar concentration
l [cm]	optical path length
E_i	energy state
ρ [mg/l]	concentration
h	Planck's constant 6.626×10^{-34} J·s

1 Introduction

The optical spectroscopic methods with their speed and great sensitivity are suitable for answering many questions in atomic and molecular research. There is possibility to measure the fluorescence from individual molecules thanks to the instruments that are able to detect a single photon together with effective lasers for nuclear movements. As a result, identities, concentrations, energies, conformations or dynamics of molecules and even their small changes can be defined. Chemical analyses such as UV/VIS spectrophotometry are the main sources of knowledge not only in chemistry itself but also in material engineering, controlling technical procedures, agriculture, food processing industry, medical diagnosis, pharmacy and in geological research [1; 2].

The building materials such as renders are naturally part of the buildings and structures together with their technological and architectural development. First mention of renders is dated in neolithic as form of earthen grease on wicker shed. Development started to grow during the Antiquity and the renders sprouted into the central Europe. Nowadays modern technologies allow us to explore the materials and their technical condition, structure and health requirements. The results help to preserve the historical buildings and improve the development of new types of renders [3].

The various types of salts can be commonly found in building materials. There are number of different ions which can be either harmless or damage the construction irrecoverably. The ions are natural components of building materials, or they are secondary introduced with water during their lifetime. The actions of salt in material depend on temperature and humidity of the environment, especially relative humidity of the air, and content of moisture in the material itself. At relative humidity higher than 75%, salts crystallize easily, on the other hand when it is under 50%, salts usually do not crystallize at all. Salts crystallize in the pore structure or on the surface due to the repeating wetting and drying of a construction during the condition change. Crystallization inside the pores is called subflorescence and on the surface efflorescence. Main reason of damage is volume change, therefore the destruction of building materials is irrecoverable. The determination of salts concentration in building materials gives the necessary information for their renovation [4].

The most used methods for determination of salts content are liquid chromatography, electric conductivity, ion-selective electrode and titration. Due to the wide range of its uses, UV/VIS spectrophotometry can also be used to measure the salt concentration in building materials. For this application, it is necessary to assess its suitability and effectiveness.

1.1 Aim of the thesis

Building materials contain number of different ions. The damage caused by salt efflorescence is irrecoverable and signifies high content of moisture in construction. The knowledge of salt concentration is essential also for renovation of buildings. There are several methods to determine the salt concentration in materials. The main aim of this bachelor's thesis is to verify the efficiency of UV/VIS spectrophotometric analysis for determination of salt leachable from building materials, specifically in eluates of lime renders. The most dangerous to the construction are nitrates, sulfates and chlorides, therefore the analysis determines these together with nitrites and ammonium.

Theoretical part is focused on UV/VIS spectrophotometry, its principle, instrumentation and optical methods in general. Further basic description of renders is introduced, together with the effect of salt presence in building materials.

Experimental part deals with the analysis of eluates from lime-based renders. The main goal during the analysis is to identify advantages and disadvantages of UV/VIS spectrophotometry and to evaluate requirements for implementation together with the time and cost efficiency.

2 Theoretical part

2.1 Analytical methods

The spectrometry is based on interaction between the electromagnetic radiation and a sample. Spectroscopic properties such as absorbance or fluorescence can define the identities, concentrations, energies, conformations, or dynamics of molecules [1; 2; 5].

2.1.1 Optical methods

Optical methods were named according to the segment of the electromagnetic spectrum that the human eye can view. They are divided into two groups: spectral and non-spectral. For the non-spectral methods, such as interferometry, polarimetry, nephelometry and turbidimetry, we are focused on a change of the properties only. The essence of the spectral methods is to measure the intensity of light as a beam of light passing through sample solution meaning to study interaction between matter and electromagnetic radiation.

The main types of spectral methods are distinguished by the nature of the interaction between the material and the energy. That includes absorption and emission spectroscopy. Another classification depends on whether the electromagnetic radiation is absorbed and emitted by atoms or molecules [1; 5].

2.1.2 Fundamental terms and concepts

Electromagnetic radiation is the radiation composed of oscillating electrical and magnetic fields, also defined as the flow of photons – particles representing a quantum of light. General properties of waves are frequency and the wavelength. Frequency (f , ν) represents the number of waves that pass a fixed point in unit time. The SI unit for frequency is the hertz (Hz). Wavelength (λ) is the distance over which the wave's shape repeats. This length is specified in metres (m), more precisely in micrometres (μm) and nanometres (nm). Properties of photon are radiant flux (ϕ), which represents energy transmitted per unit time and irradiance (I) as the radiant flux received by a surface per unit area [1; 5].

Electromagnetic spectrum as a distribution of electromagnetic radiation according to wavelength with a range from 10^{-13} to 10^6 m. Visible light range is from about 380 nm to about 750 nm, with a shorter wavelength we are getting to ultraviolet, X-ray and gamma ray area and in a opposite direction to the longer wavelength into the infrared, microwave and

radio area. Particular kinds of electromagnetic spectrum together with their wavelengths and frequencies are demonstrated in *Figure 1* [5].

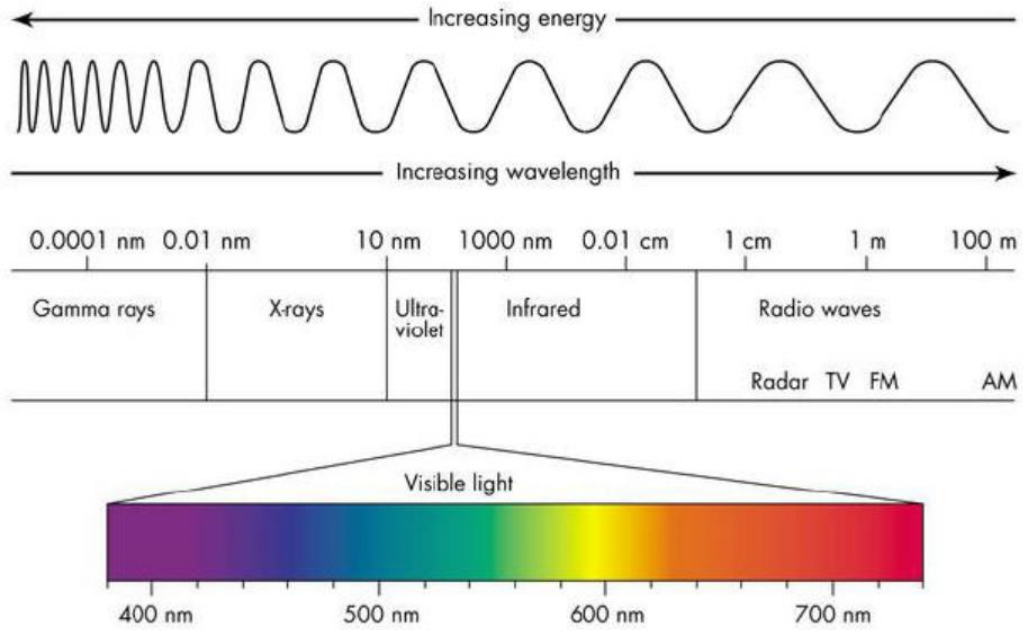


Fig. 1: Electromagnetic spectrum [6]

Transmittance T is defined as the ratio of the transmitted intensity I over the incident intensity I_0 . This property can be expressed by *equation 1*.

$$T = \frac{I}{I_0} \quad (1)$$

Transmittance takes values between 0 and 1 and it is presented as a percentage transmittance [5].

Absorbance A is explicated as a negative logarithm of transmittance expressed by *equation 2*.

$$A = -\log T = \log \frac{I_0}{I} \quad (2)$$

Absorbance is dimensionless quantity and takes values between 0 and ∞ [5].

Lambert-Beer law, also known as Beer-Lambert-Bouguer law defines the absorption of light by an absorbing substance together with the properties of that substance and is expressed by *equation 3*.

$$A = \varepsilon \cdot c \cdot l \quad (3)$$

where A is absorbance, ε is molar absorption coefficient [$\text{dm}^3/(\text{mol}\cdot\text{cm})$], c is molar concentration [mol/dm^3] and l is optical path length [cm]. The molar absorption coefficient is given as a constant for each molecule.

The Lambert-Beer law declares that there is a linear relationship between the concentration and the absorbance of the solution, therefore it is possible to calculate concentration by measuring absorbance. The law only applies when radiation is monochromatic, solution is dilute (its concentration is under $10^{-2} \text{ mol}/\text{dm}^3$) and there is no condition change during the measurement [2; 7].

2.1.3 UV/VIS spectrophotometry

UV/VIS spectrophotometry is molecular, absorption spectroscopy which uses light over the ultraviolet and visible range of electromagnetic radiation spectrum that means 180-780 nm. Substances with wavelength under 380 nm appear as achromatic. Radiation with wavelength under 200 nm is known as “vacuum-ultraviolet region” and requires evacuated apparatus. Spectrophotometry is one of the most useful methods of quantitative analysis in numerous fields such as chemistry, physics, biochemistry etc. [5; 8].

2.1.3.1 Principles

The basic principle of spectroscopy is a measurement of how much a substance absorbs or transmits light over a certain range of wavelength.

The mathematical-physical basis of light absorption is formed by the Lambert-Beer law (*Chapter 2.1.2 – Fundamental terms and concepts*).

Optical spectroscopy in general is based on the Bohr-Einstein frequency relationship expressed by *equation 4*.

$$\Delta E = E_1 - E_0 = h \cdot \nu \quad (4)$$

where E_i is atomic or molecular energy state, ν is frequency of the electromagnetic radiation and h is Planck's constant ($6.626 \times 10^{-34} \text{ J}\cdot\text{s}$). In spectroscopy it is suitable to work with wavenumber $\sim \nu$ instead of frequency ν . The *equation 4* transforms as:

$$\Delta E = E_1 - E_0 = h \cdot c \cdot \sim \nu \quad (5)$$

Absorbed or emitted radiation can be specified by energy-level differences outward from *equation 6*.

$$\sim\nu = \frac{\Delta E}{h.c} = \frac{E_1}{h.c} - \frac{E_0}{h.c} = T_2 - T_1 \quad (6)$$

where T_i is term value (= energy level).

In normal conditions molecules are in ground energy state, this energy is defined as sum of electronic (E_e), vibrational (E_v) and rotational (E_r) energy expressed in *equation 7*.

$$E_0 = E_e + E_v + E_r \quad (7)$$

By absorption of quantum of photons molecule transits from ground to excited state. There are two types of transition, when molecule transits to a higher energy level and photons are absorbed, we talk about the absorption, opposite, when molecule drops to a lower energy level due to the interaction of photon and excited electron, is called emission (*Figure 2*).

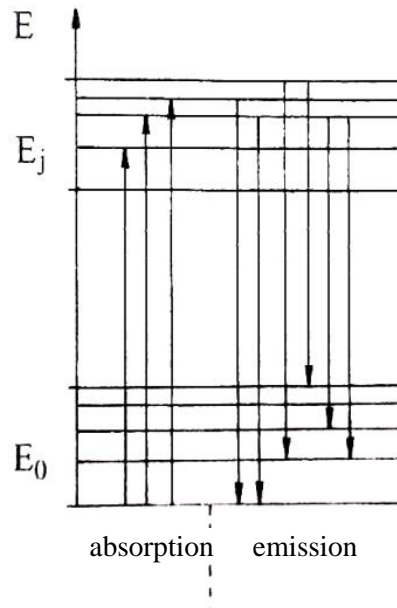


Fig. 2: Absorption and emission [5]

An excited state has shorter lifetime than ground state, lifetime is defined in 10^{-9} s. Molecules transit back to the ground state by de-excitation process. Energy and process itself is described by equation 4. Electronic transitions caused by the absorption of light wage from different vibrational and rotational ground states to any vibrational and rotational excited states. Energy necessary for electronic states ($\Delta E_e \sim 150-600$ kJ/mol) is much bigger than energy for vibrational (2-60 kJ/mol) and rotational (3 kJ/mol) states. Simultaneously

with electronic state transition there is always excitation of vibrational and rotational energy levels [7; 9].

The absorption of UV/VIS radiation corresponds to the excitation of outer electrons, and we consider three types of electronic transitions, involving:

- π , σ and n electrons
- charge-transfer (CT) electrons
- d and f electrons

In organic molecules absorption is restricted to certain functional groups, which are called chromophores that carry valence electrons. The spectrum is complex because the superposition of rotational and vibrational transitions on the electronic transitions gives a combination of overlapping lines. These lines appear as a continuous absorption band. Various types of transitions are displayed in *Figure 3*.

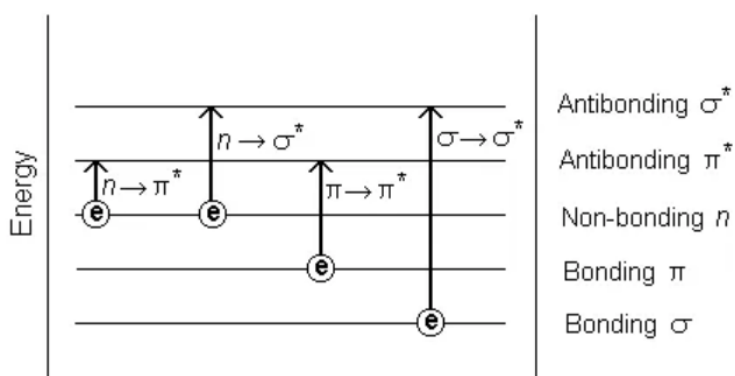


Fig. 3: Types of electronic transitions [10]

$\sigma \rightarrow \sigma^*$ transitions are not typical for UV/VIS spectrophotometry. An electron in a bonding σ orbital is excited to the corresponding orbital.

$n \rightarrow \sigma^*$ transitions are not typical for UV/VIS as well, because number of organic functional groups with this transition is very small. For this transition compound needs to contain atoms with lone pairs.

$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are typical for UV/VIS because the absorption peaks fall in convenient region of the spectrum (200 - 700 nm). The molecule needs an unsaturated group to provide the π electrons.

Charge-transfer absorption is for inorganic and organic pairs called charge-transfer complexes. One of the components behaves as a donor and another as an acceptor. Absorption of radiation then involves the transfer of an electron [11].

2.1.3.2 Instrumentation

An instrument that measures the amount of light absorbed by a sample is called a spectrophotometer. The spectrophotometer was invented in 1940 by scientist Arnold J. Beckman. Every type of spectrophotometer has the same principle and essential components such as radiant energy source, monochromator, cuvettes, photosensitive detector, and associated readout system. Technique is to measure light intensity as a function of wavelength. *Figure 4* illustrates the basic structure of spectrophotometers, in general, light beam diffracts into a spectrum of wavelengths, then it detects the intensities with charge-coupled device and displays the results.

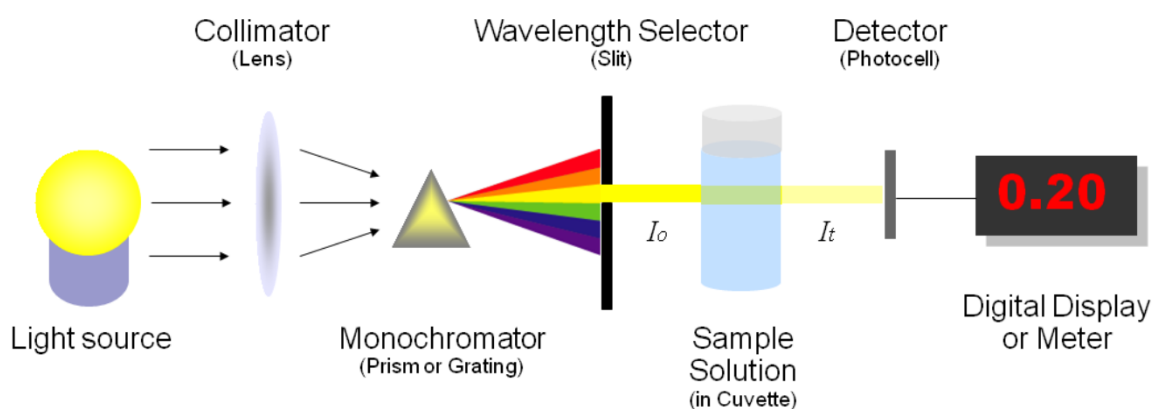


Fig. 4: Basic structure of spectrophotometers [12]

There are two types of spectrophotometers – single beam and double beam spectrophotometer. Using the single beam, the light travels in one direction and solution and blank are read in the same. Double beam has two photocells – two paths. One beam for the reference and the other for a sample solution [8].

As a radiant energy source for the ultraviolet region is used the hydrogen or deuterium lamp, for the visible region of the spectrum it is tungsten filament lamp or carbon arc. Monochromatic radiation is gained by using dispersing elements such as gratings or prisms. The transport vessels which hold the sample are known as cuvettes. Cuvettes should not absorb in the same region as the solution, so they are made up of ordinary glass or quartz. Most detection devices depend on the photoelectric effect. They should have high sensitivity, short response time, long-term stability and electric signal for a readout apparatus. As a result electronic signals are generated and need to be translated into a form that is easy to interpret by using amplifiers [5; 13].

Before measurement itself, spectrophotometer calibration is made. Calibration is a process in which researcher uses a calibration standard to examine the accuracy of the light source. It is essential for correct operation of spectrophotometer and follow-up measurements.

2.1.3.3 Applications

UV/VIS spectrophotometry is used in quantitative and qualitative analysis for organic and inorganic compounds. Major fields are following medicine, biochemistry, clinical research, food industry and ecology. Advantages of spectrophotometry are rapidity, simplicity, sensitivity of measurement and low expenses. Main use is in quantitative analysis because qualitative is ambiguous and needs following measurements such as IR or NMR. Particular application is for example determination of the concentration of coloured as well as colourless mixtures by measuring its absorbance, detection of impurities, molecular weight determination of compounds, respiratory gas analysis in hospitals and more [1; 5; 13].

2.2 Renders

The renders as well as the other building materials have highly developed over the past years. They have aesthetic function as final finish of the surface, and they have to comply the high technical demands at the same time. There is wide variability and specialization on the render market. The types of renders according to the binding agent are lime, lime-cement, cement, gypsum, clay as the mineral plasters and silicone, acrylic, silicate as the organic plasters [14].

2.2.1 Salts

The salt efflorescence is the main evidence of humidity in objects. Object is devaluated aesthetically, and efflorescence contributes to complete damage of renders. Critical parts are plinths, damaged gutters, and downpipes. There is a large number of different ions in every building material such as render. The origin of the ions can be either natural or secondary introduced in the form of water solution. The salts are transported by capillary forces. Salts crystallize due to the water evaporation during the condition change of environment. Crystallization takes place on the surface (efflorescence) or inside the pores (subflorescence). Example of efflorescence on *Figure 5*. Not all salts are damaging to the construction. The most dangerous salts are nitrates, sulfates and chlorides. Nitrates origin

from fertilizers or as a result of biological oxidation of organic compounds. Sulfates also come from fertilizers and further as effect of acid rain (from SO_2 contained in atmosphere). Chlorides are part of salts used for winter maintenance. Most common origin for all ions is also as a part of building material itself and in ground water. The danger presents volume change during the crystallization, and destruction is proportional to the crystallization pressure. Values of the pressure can be for example 23.5 MPa for mirabilite (also known as Glauber's salt – $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and 94 MPa for gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Renders are damaged irrecoverably. There is no opportunity for temporary renovation, renders need to be removed along with base masonry and then renovation render is applied [3; 4].

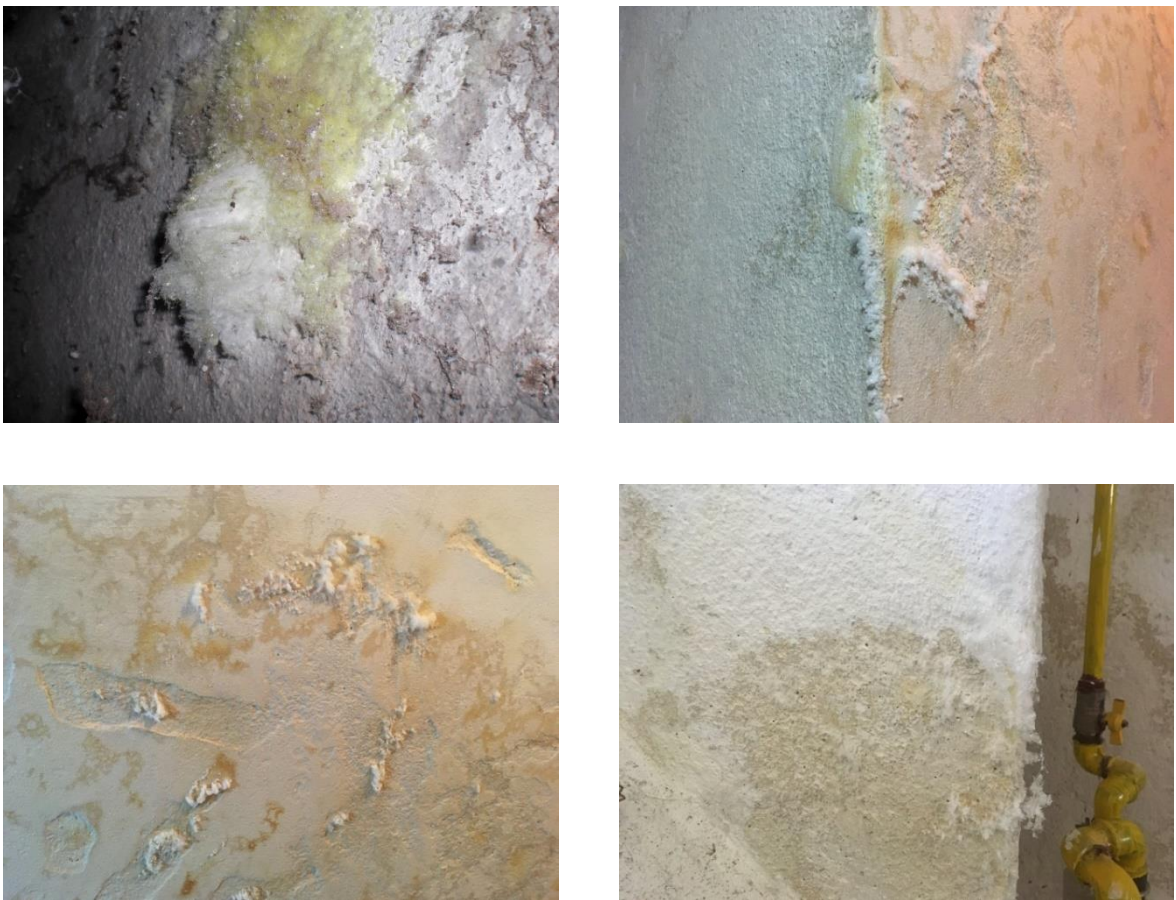


Fig. 5: Examples of efflorescence [15]

2.2.2 Renovation renders

The renovation renders are used for the surface treatment of humid masonry during the rehabilitation. They are able to eliminate the rise by capillary action due to their porous structure and inner hydrophobicity.

WTA directive 2-9-04/D [16] for renovation renders declares product qualities, especially low diffusion resistance. WTA renovation render is dry-mixed mortar significant for its high

porosity and vapour permeability together with very low capillary action. There is also WTA base render for levelling uneven surfaces, which has lower requirements. Moisture-absorbing and porous renders are made for reduction the amount of contained salts and then after two years they are removed. More suitable are multilayer structures. Lifetime of renovation renders is relatively long because the capacity for salts storing after fifteen years is still undepleted. According to WTA directive the diffusion equivalent air layer thickness of surface treatment should be lower than 0.2 metre ($r_d < 0.2 \text{ m}$), which is axiomatic for producers of high-quality facade colours. Absorbing power of surface treatment is the second problem, from architectural view and from natural ageing process itself. Absorbing power of facade colour should not be higher than absorbing power of base.

Indoor application of renovation renders eliminates danger of mould growth, even in surroundings with very high relative humidity. Implementation of renovation renders is very demanding process, in which precise terms of application should be followed [14].

3 Experimental part

3.1 Instrumentation

Spectrophotometer

For UV/VIS spectrophotometry measurement was used Spectrophotometer Thermo Scientific GENESYS 30 Vis (*Figure 6*). The instrument is equipped with single-beam optical system and wide length range 325 – 1100 nm with precision ± 2 nm. Components of the instruments are 5inch color screen with push-button keypad, single cell measurement with standard cell holder for cuvettes and thermal printer. The data can be exported on USB in a text format or there is possibility to operate by PC software [17].



Fig. 6: Spectrophotometer Thermo Scientific GENESYS 30 Vis

Analytical balances

For measuring weight, OHAUS Pioneer analytical balances were used (*Figure 7*). The balances have precision ± 0.002 g, readability 0.001 g and wide range of units such as gram, pound and ounce [18].



Fig. 7: OHAUS Pioneer analytical balances

Heating plate

For heating, the water Velp Scientifica REC hot plate was used (*Figure 8*). Plate is made from ceramic, which resists acids, bases and solvents, and is ambient to 550 °C. Control panel is separated from heating plate and has high visibility LED display of temperature [19].

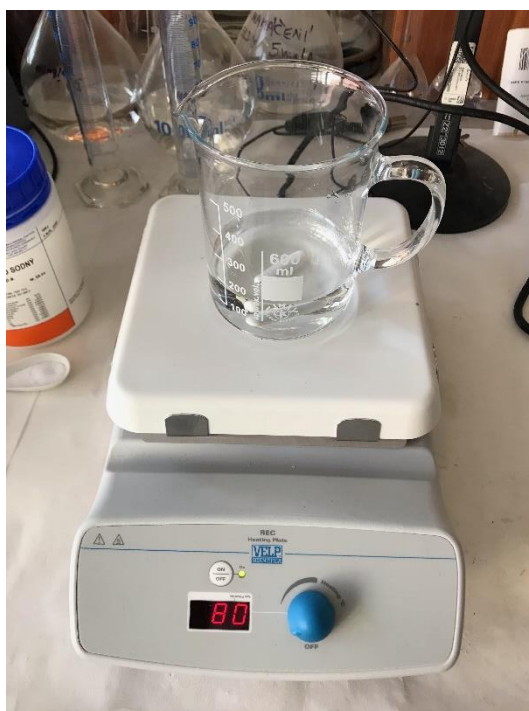


Fig. 8: Velp Scientifica REC Hot Plate

Incubator

For incubation of solutions during the analysis was used IKA Incubator shaker KS 4000 ic control (*Figure 9*). Incubator has large LED display for speed, temperature and time settings and controls with antimicrobial coating for reduction of bacteria. Unit stops automatically when hood is lifted. Incubator can be controlled and documented using lab WorldSoft software. Maximum speed range is 500 rpm (revolutions per minute) [20].



Fig. 9: IKA Incubator shaker KS 4000 ic control

Magnetic plate stirrer

For mixing solutions IKA Color Squid IKAMAG magnetic plate stirrer was used (*Figure 10*). Stirrer is made of recyclable materials with glass top providing good chemical resistance and has electronically controlled motor with speed range 0-1500 rpm. Stirring volume is 800 ml [21].



Fig. 10: IKA Color Squid Harry Magnetic Stirrer

3.2 Characterization of samples

Subjects of analysis were ten eluates = samples of lime render dissolved in water. The samples were taken in 2017 from historic bishop residence buildings in Litoměřice. The area of bishop residence consists of bishop residence itself, main entrance gate, portal to court, gate between forecourt and cattle house, brick object number 1 and 2, brick cattle house number 3 and 4 and former brick stable. Some of the buildings were partly reconstructed [22]. The samples were chosen for spectrophotometric analysis considering cardinal direction, condition and height above ground. Information about samples in detail are demonstrated in *Table 1*.

Tab. 1: Characterization of samples.

Number	Object	Sampling place	Plaster condition	Height above ground [mm]
1	Former brick stable	N wing: E outside wall - interior	better with height gradient	1150
2	Brick object n. 1	S outside wall - down	damaged	
3	Brick object n. 1	S outside wall - up	good	
4	Main entrance gate	W main entrance gate	good	
5	Brick object n. 2	S outside wall - down	damaged	
6	Brick cattle house n. 3	E outside wall - down	damaged	
7	Former brick stable	E wing: W outside wall	better with height gradient	350
8	Brick cattle house n. 3	E outside wall - up	good	
9	Former brick stable	N wing: E outside wall - interior	better with height gradient	150
10	Former brick stable	N wing: E outside wall - interior	better with height gradient	650

* *N = North; S = South; W = West; E = East*

Preparation of eluates started by weighing 2 g of sample with fraction <0.063 mm using analytical balances OHAUS Voyager with precision ± 0.001 g. Sample was put into the plastic weighing bottles of 20 ml volume and 20 ml of redistilled water was added. This suspension was shaken for 30 s and then put into IKA KS 501 Orbital Digital Platform Shaker for 24 hours with frequency 230 rpm [22].

3.3 Analysis

The analysis of eluates of renders was made according to the standard ISO 15923-1 [23]. Subjects of analysis were these ions: ammonium, sulfate, nitrite, nitrate and chloride. For all measurements was used calibration curve method, which is a general method for determining the concentration of substance and presents relation between the absorbance and concentration of analysed ion. Its principle and construction are demonstrated in Chapter 3.3.1 Determination of sulfate by the turbidimetric method.

3.3.1 Determination of sulfate by the turbidimetric method

3.3.1.1 Principle

In an acid environment sulfate forms a precipitate with barium chloride. Measuring of the sulfate content is based on the resulting turbidity. The absorbance is measured at 540 nm [23].

3.3.1.2 Used chemicals

Gelatine – Lach-Ner, s.r.o.

Barium chloride [BaCl₂·2H₂O] – Penta s.r.o.

Sodium chloride [NaCl] – Penta s.r.o.

Concentrated hydrochloric acid [HCl] – Lach-Ner, s.r.o.

Sodium sulfate [Na₂SO₄] – Penta s.r.o.

Distilled water

3.3.1.3 Preparation of reagents

For this procedure two reagents were prepared. **Turbidimetric reagent**, starting with 0.125 g of gelatine dissolved in 200 ml of hot water (80 °C). Gelatine as well as other grain materials was weighed on OHAUS analytical balances (*Figure 7*). Water was warmed on a heating plate (*Figure 8*) and then mixed with gelatine for 1 hour on a magnetic stirrer plate (*Figure 10*). Dissolved gelatine was transferred in a 500 ml measuring flask and then 5 g of barium chloride, 5 g of sodium chloride and 2.5 ml of concentrated hydrochloric acid was added. Mixture was filled to the mark with water. For **primary calibration standard sulfate** of concentration 2000 mg/l, sodium sulfate was desiccated for 2 hours at 105 °C and then 2.957 g of it was dissolved in 250 ml of water and filled to the mark in 1 l measuring flask.

3.3.1.4 Calibration and analysis

Calibration standards of concentration 5 mg/l; 10 mg/l; 50 mg/l; 100 mg/l; 150 mg/l and 200 mg/l were prepared by dilution of primary calibration standard ($\rho = 2000$ mg/l) with distilled water. Standards were mixed in 100 ml measuring flasks (*Figure 11*). Volume of primary calibration standard was based on *equation 8*. Dilution of solutions is displayed in *Table 2*.

$$c_1 \cdot V_1 = c_2 \cdot V_2 \quad (8)$$

Tab. 2: Dilution of primary calibration standard sulfate ($\rho = 2000$ mg/l)

	Concentration [mg/l]	Volume of primary calibration standard [ml]
Standard 1	5	0.25
Standard 2	10	0.5
Standard 3	50	2.5
Standard 4	100	5
Standard 5	150	7.5
Standard 6	200	10



Fig. 11: Calibration standards in 100 ml measuring flasks

Blank, which is a sample that contains everything except of the analyte of interest, and prepared standards were analysed as describe below and calibration curve was constructed.

Measured absorbances of calibration standards are displayed in *Table 3*. After standards measurement and construction of calibration curve (*Figure 12*) analysis of eluates was made.

Tab. 3: Calibration data

	Concentration [mg/l]	Absorbance
Standard 1	5	0.011
Standard 2	10	0.022
Standard 3	50	0.175
Standard 4	100	0.427
Standard 5	150	0.579
Standard 6	200	0.750

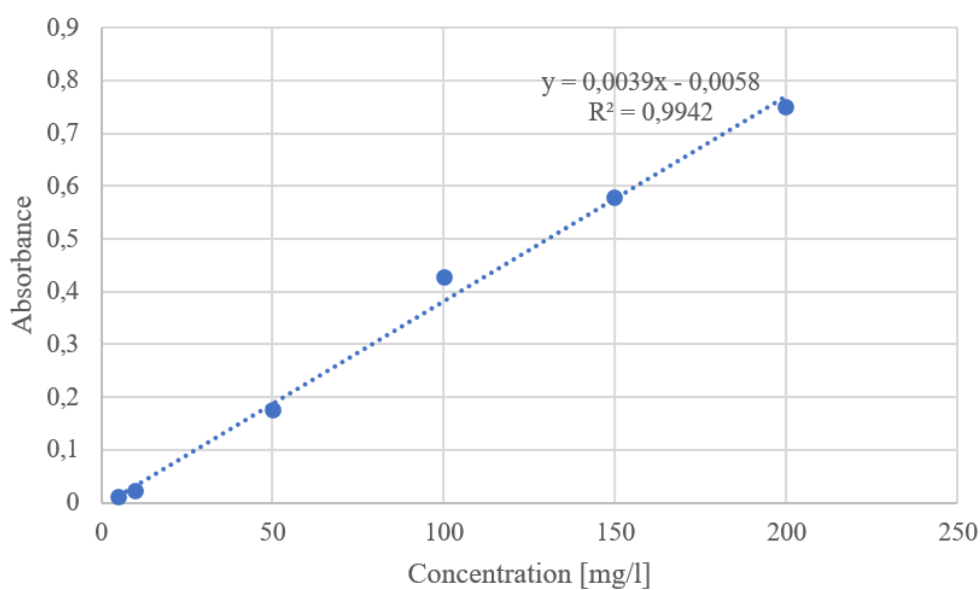


Fig. 12: Calibration curve

The analysis started with preparation of measuring solution made of 1 part (= 2 ml) of sample and 1 part (= 2 ml) of turbidimetric reagent. Mixture was put into the incubator with temperature 30 °C for 240 s. After incubation measuring solution was poured into 4 ml cuvette and absorbance at 540 nm was measured in the spectrophotometer.

3.3.2 Determination of ammonium

3.3.2.1 Principle

Ammonium interacts with hypochlorite and salicylate at a pH around 12.6, along with sodium nitroprusside as a catalyst, to produce a compound with a blue colour. The absorbance is measured at 660 nm [23].

3.3.2.2 Used chemicals

Sodium salicylate [$C_7H_5O_3Na$] – Lach-Ner, s.r.o.

Sodium citrate [$C_6H_5Na_3O_7 \cdot 2H_2O$] – Lach-Ner, s.r.o.

Sodium nitroprusside [$Na_2(Fe(CN)_5NO) \cdot 2H_2O$] – Lach-Ner, s.r.o.

Sodium hydroxide [NaOH] – Lach-Ner, s.r.o.

Sodium dichloroisocyanurate [$Cl_2Na(NCO)_3 \cdot 2H_2O$] – Sigma-Aldrich s.r.o.

Ammonium sulfate [$(NH_4)_2SO_4$] – Lach-Ner, s.r.o.

Distilled water

3.3.2.3 Preparation of reagents

For the determination of ammonium three reagents were prepared. First was **sodium nitroprusside reagent**. In a 250 ml measuring flask was dissolved 32.5 g of sodium salicylate and 32.5 g of sodium citrate in 200 ml of water. pH was under 8, so acidifying with nitric acid was not necessary. At last, 0.243 g of sodium nitroprusside was added, dissolved, and measuring flask filled to the mark with water. For **DIC reagent** again in a 250 ml measuring flask 8 g of sodium hydroxide was dissolved in 200 ml of water, then 0.5 g of sodium dichloroisocyanurate was added and dissolved. Mixture was filled to the mark with water. Before measurement, the calibration needs to be done. For **primary calibration standard ammonium** 1.415 g of ammonium sulfate was dissolved in 750 ml of water and then 1 l calibrated flask was filled to the mark. This standard has concentration $\rho_N = 300$ mg/l.

3.3.2.4 Calibration and analysis

Dilute solutions from primary calibration standard of concentration: 0.05 mg/l; 0.1 mg/l; 0.2 mg/l; 0.5 mg/l; 1.0 mg/l and 2.0 mg/l were made, and the calibration curve was constructed, using analysis of a blank and six solutions.

For analysis incubator with temperature 35 °C was used. Measuring solution was made up of 2 parts (=2 ml) of sample, 1 part (=1 ml) of sodium nitroprusside reagent and 1 part (=1 ml) of DIC reagent. Mixed solution was incubated for 480 s. After the incubation time, the absorbance was measured.

3.3.3 Determination of nitrite

3.3.3.1 Principle

Nitrite reacts with sulfanilamide and N-(1-naphthyl)ethylenediamine dihydrochloride in an acid environment to form a diazide compound with a red colour. The absorbance is measured at 540 nm [23].

3.3.3.2 Used chemicals

Phosphoric acid 85% [H₃PO₄] – Penta s.r.o.

Sulfanilamide [C₆H₈N₂O₂S] – Lach-Ner, s.r.o.

N-(1-naphthyl)ethylenediamine dihydrochloride [C₁₂H₁₆Cl₂N₂] – Lach-Ner, s.r.o.

Sodium nitrite [NaNO₂] – Lach-Ner, s.r.o.

Distilled water

3.3.3.3 Preparation of reagents

For this analysis, **NED reagent** was prepared in a 1 l measuring flask in a following order: 50 ml of phosphoric acid in 500 ml of water, 5 g of sulfanilamide, 0.25 g of NED and filling to the mark with water. This solution was stored in a dark bottle and cold. As next **primary calibration standard nitrite** of concentration $\rho_N = 200$ mg/l needed to be done. The preparation started with desiccation of sodium nitrate for 1 hour in 105 °C and cooling it in an exsiccator for 45 minutes. 0.985 g of sodium nitrate was dissolved in 750 ml of water and again in a 1 l measuring flask filled to the mark with water.

3.3.3.4 Calibration and analysis

The calibration curve was again first order. Primary calibration standard was diluted in concentrations 0.01 mg/l; 0.05 mg/l; 0.1 mg/l; 0.2 mg/l; 0.3 mg/l and 0.6 mg/l. Analysis of a blank and six solutions was made.

The incubation temperature was 30 °C. Measuring solution was made of 1 part of sample (= 2 ml) and 1 part (= 2 ml) of NED reagent, mixture was incubated for 360 s and then the absorbance was measured.

3.3.4 Determination of the sum of nitrate and nitrite by hydrazine method

3.3.4.1 Principle

The determination is based on reduction of nitrate to nitrite with hydrazine sulfate. Nitrite produced by reaction and nitrite in the sample react with sulfanilamide and N-(1-naphthyl)ethylenediamine dihydrochloride (NED) to produce a diazide compound with a red colour. The absorbance is measured at 540 nm [23].

3.3.4.2 Used chemicals

Copper sulfate [$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$] – Lach-Ner

Zinc sulfate [$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$] – Lach-Ner

Sodium hydroxide [NaOH] – Lach-Ner

Hydrazine sulfate [$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$] – Lach-Ner, s.r.o.

Phosphoric acid 85% [H_3PO_4] – Penta s.r.o.

Sulfanilamide [$\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{S}$] – Lach-Ner, s.r.o.

N-(1-naphthyl)ethylenediamine dihydrochloride [$\text{C}_{12}\text{H}_{16}\text{Cl}_2\text{N}_2$] – Lach-Ner, s.r.o.

Potassium nitrate [KNO_3] – Lach-Ner, s.r.o.

Distilled water

3.3.4.3 Preparation of reagents

First, three solutions were prepared. **Copper sulfate solution** (3.9 g/l) prepared by dissolving 0.39 g of copper sulfate in 100 ml of water, **zinc sulfate solution** (45 g/l), where 4.5 g of zinc sulfate was dissolved in 100 ml of water and **sodium hydroxide solution** (8 g/l) prepared again by dissolving 0.8 g of sodium hydroxide in 100 ml of water. The preparation of **reduction reagent** started with dissolving 0.163 g of hydrazine sulfate in 200 ml of water, then 0.375 ml of copper sulfate solution and 2.5 ml of zinc sulfate solution were added. 250 ml measuring flask was filled to the mark with water. **NED reagent** from determination of nitrite was used. Last reagent needed was **primary calibration standard nitrate** of concentration $\rho_{\text{N}} = 600 \text{ mg/l}$. Preparation started with desiccation of potassium nitrate for

2 hours at 105 °C and cooling it in an exsiccator for 45 minutes. 4.331 g of potassium nitrate was dissolved in 750 ml of water and 1 l measuring flask was filled to the mark.

3.3.4.4 Calibration and analysis

The calibration curve was first order. Primary calibration standard was diluted in concentrations 0.1 mg/l; 0.5 mg/l; 1 mg/l; 2 mg/l; 3 mg/l and 6 mg/l. Analysis of a blank and six solutions was made.

The incubation temperature was 35 °C. Measuring solution was made of 1 part (= 1 ml) of sodium hydroxide solution and 1 part (= 1 ml) of sample. This mixture was incubated for 180 s. Then 1 part (= 1 ml) of reduction reagent was added and incubated for 420 s. Final addition of 1 part (= 1 ml) of NED reagent was done and incubated for 300 s. Whole procedure took 15 minutes. Samples were analysed by spectrophotometry in 4 ml volume cuvettes at 540 nm.

3.3.5 Determination of chloride by the thiocyanate method

3.3.5.1 Principle

Determination is based on reaction of chloride with mercury (II) thiocyanate forming non-ionized mercury (II) chloride and free thiocyanate, which forms a red complex with iron (III). The absorbance is measured at 480 nm [23].

3.3.5.2 Used chemicals

Mercury thiocyanate [Hg(SCN)₂] – Sigma-Aldrich s.r.o.

Methanol [CH₃OH] – Chemapol, a.s.

Iron nitrate [Fe(NO₃)₃·9H₂O] – Sigma-Aldrich s.r.o.

Concentrated nitric acid [HNO₃] – Chemapol, a.s.

Sodium chloride [NaCl] – Penta s.r.o.

Distilled water

3.3.5.3 Preparation of reagents

For the thiocyanate method four reagents were prepared. **Mercury thiocyanate solution** by dissolving 0.208 g of mercury thiocyanate in 50 ml of methanol and **iron nitrate solution** by dissolving 10.1 g of iron nitrate in 35 ml of water, adding 2.22 ml of concentrated nitric

acid and filling to the mark of 50 ml measuring flask with water. From 50 ml of mercury thiocyanate solution and 50 ml of iron nitrate solution, **chromogenic reagent** was made in a 500 ml measuring flask filled to the mark with water. These reagents should be stored in a dark bottle at room temperature. **Primary calibration standard chloride** with concentration 50 g/l was made by dissolving 41.21 g of sodium chloride in a 500 ml measuring flask. Sodium chloride was desiccated over night at 105 °C and cooled in an exsiccator for 45 minutes before the preparation. This standard should be stored at 2 °C to 8 °C.

3.3.5.4 Calibration and analysis

Primary calibration standard was diluted in concentrations 5 mg/l; 10 mg/l; 50 mg/l; 100 mg/l; 200 mg/l and 400 mg/l. Analysis of a blank and six solutions was made, and calibration curve was constructed. In *Figure 13* there is blank sample at back row, which is least colored and calibration standards from lowest concentration at the left. As the concentration rises, standards are more colored.

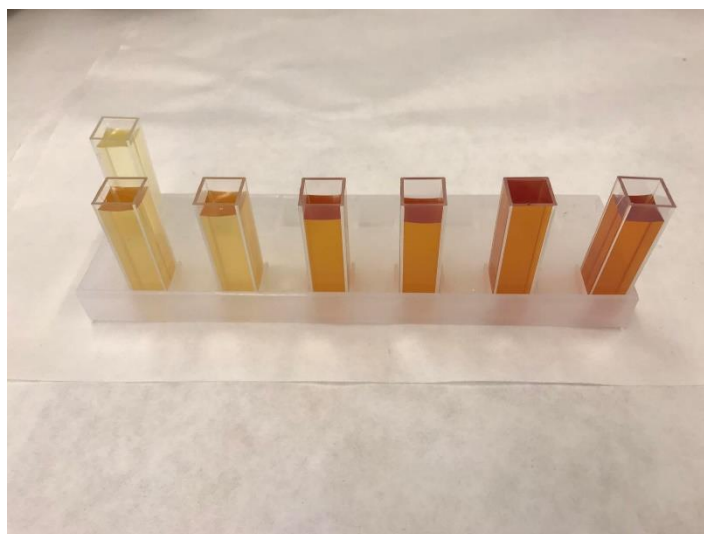


Fig. 13: Calibration solutions – back left: blank; front from left: concentrations upwardly

The analysis was accomplished at room temperature. Measuring solution was made up of 6 parts (= 6 ml) of chromogenic reagent which was incubated for 240 s and 1 part (= 1 ml) of sample incubated for 180 s. Whole procedure took 7 minutes. Absorbance at 480 nm was measured.

3.4 Evaluation and discussion of results

3.4.1 Sulfate

The concentration of sulfates in samples was very high, six measurements were outside the calibration range, but not with absorbance over 3, so the results are valid. The sulfate content was obvious from the resulting turbidity created during the analysis. Sulfates form a precipitate with barium chloride in an acid environment. The scale of turbidity is apparent from *Figure 14*. Results of measurement are summarized in *Table 4*.

Tab. 4: Results of analysis of sulfates

Sample	Absorbance	Concentration [mg/l]
1	1.430	372.30
2	2.059	536.06
3	2.006	522.26
4	1.648	429.06
5	2.113	550.12
6	1.929	502.21
7	0.165	42.96
8	2.245	584.48
9	2.148	559.23
10	2.050	533.72



Fig. 14: Measuring solutions – back line from left: 1-5, front line from left: 6-10

3.4.2 Ammonium

Reaction between ammonium and hypochloride, salicylate and sodium nitroprusside forms a compound with a blue colour. The coloration is shown on *Figure 15*. Six of ten samples were out of the calibration range (concentration is higher than 2 mg/l) and three of them could not be evaluated by the spectrophotometer (absorbance higher than 3 is displayed as error and the data are not accurate). This was due to the high concentration of calcium cations in eluates from lime-based renders, which interfere with the determination of ammonium. Interference by calcium cations was not masked by citrate because its complexing capacity was exceeded. Results of spectrophotometric analysis are displayed in *Table 5* - invalid values are bolded. Nevertheless, as the calcium content strongly affects this measurement, it is not possible to consider any obtained results to be correct. It was not possible to prevent this by carrying out a distillation (as proposed in the standard [23]) because of the low volume of samples. In conclusion this method of determination of ammonium is not suitable for lime-based renders.

Tab. 5: Results of analysis of ammonium

Sample	Absorbance	Concentration [mg/l N]	Concentration [mg/l NH ₄]
1	4.046	5.49	7.06
2	1.675	2.27	2.92
3	0.193	0.26	0.34
4	0.769	1.04	1.34
5	1.007	1.37	1.76
6	1.038	1.41	1.81
7	4.046	5.49	7.06
8	2.159	2.93	3.76
9	4.046	5.49	7.06
10	2.415	3.28	4.21

**Invalid values*

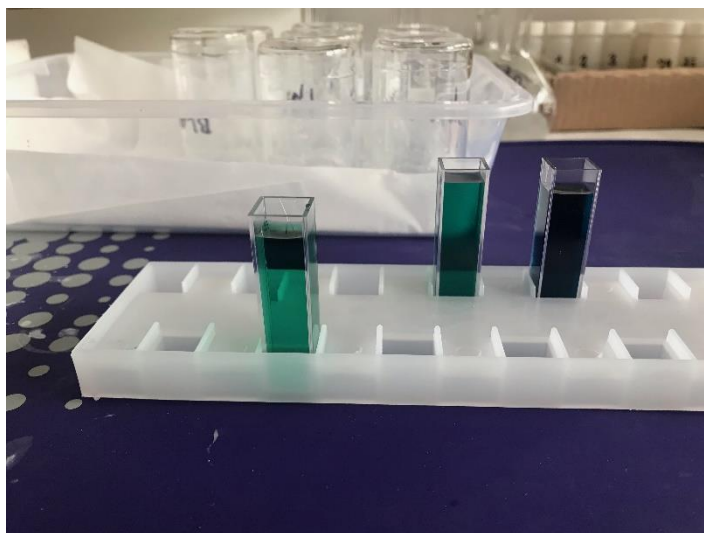


Fig. 15: Measuring solutions – from left: calibration standard; 10; 9

3.4.3 Nitrite

Three samples were out of the calibration range, which means that absorbance was higher than 3 and the result was displayed as error, so given number of absorbance and concentration was invalid. As a solution, dilution with distilled water was made for sample 1, 6 and 9, following 0.5 ml of a sample and filled to the mark of 5 ml measuring flask with distilled water. For a sample 6, dilution was made again with 0.5 ml of diluted sample and again filled to the mark of 5 ml measuring flask with water. Results of concentration were recalculated. Concentration of nitrite was calculated with conversion factor 3.285 according to the standard [23]. *Tables 6 and 7* show that the concentration of nitrite in solutions was low.

Tab. 6: Results of analysis of nitrite

Sample	Absorbance	Concentration [mg/l N]	Concentration [mg/l NO ₂]
1	>3	Error	-
2	0.440	0.111	0.37
3	0.353	0.089	0.29
4	0.213	0.054	0.18
5	0.667	0.168	0.55
6	>3	Error	-
7	0.012	0.003	0.01
8	2.417	0.608	2.00
9	>3	Error	-
10	0.588	0.148	0.47

Tab. 7: Results for diluted solutions

Sample	Absorbance	Concentration [mg/l N]	Recalculated concentration [mg/l N]	Concentration [mg/l NO ₂]
1	2.055	0.517	5.17	16.98
6	0.371	0.093	9.3	30.55
9	0.385	0.097	0.97	3.19

3.4.4 The sum of nitrate and nitrite

During the reaction of hydrazine method diazine compound with a red colour is formed. The coloration is shown in *Figure 16*. Three samples were out of the calibration range. Dilution with distilled water was made for sample 1, 6 and 8. For a sample 6, dilution was made again. Dilution was described in Chapter 3.4.3 Nitrite. Results of concentration were recalculated. The obtained values are displayed in *Tables 8 and 9*.

Tab. 8: Results of analysis of the sum of nitrate and nitrite

Sample	Absorbance	Concentration [mg/l N]
1	>3	Error
2	0.443	0.937
3	0.470	0.994
4	0.516	1.091
5	0.451	0.953
6	>3	Error
7	0.048	0.101
8	>3	Error
9	1.367	2.890
10	0.231	0.488

Tab. 9: Results of diluted solutions

Sample	Absorbance	Concentration [mg/l N]	Recalculated concentration [mg/l N]
1	1.153	2.438	24.38
6	1.455	3.076	307.60
8	1.041	2.201	22.01

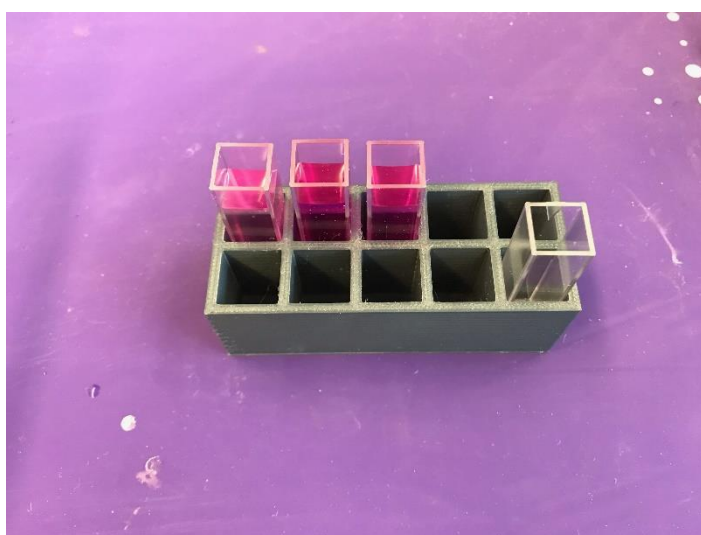


Fig. 16: Measuring solutions – from left: 2,3,4

Hydrazine method determinates the sum of nitrate and nitrite. To determine nitrate, the nitrite value was subtracted from the result obtained by using this procedure. Nitrite value

was taken from *Chapter 3.3.3 - Determination of nitrite*. The calculation was made with conversion factor 4.427 according to the standard [23]. The concentration of nitrate was higher than nitrite.

Tab. 10: Calculation of nitrate values

Sample	Concentration			
	$\Sigma\text{NO}_2^- + \text{NO}_3^-$ [mg/l N]	NO_2^- [mg/l N]	NO_3^- [mg/l N]	NO_3^- [mg/l NO_3]
1	24.380	5.170	19.210	85.04
2	0.937	0.111	0.826	3.66
3	0.994	0.089	0.905	4.01
4	1.091	0.054	1.037	4.59
5	0.953	0.168	0.785	3.48
6	307.600	9.300	298.300	1320.57
7	0.101	0.003	0.098	0.43
8	22.010	0.608	21.402	94.75
9	2.890	0.970	1.920	8.50
10	0.488	0.148	0.340	1.51

3.4.5 Chloride

The concentration of chloride was very high as expected. All measurements were in calibration range and correction was not needed. Chlorides react with mercury (II) thiocyanate and originated free thiocyanate forms a red complex with iron. The coloration of measuring samples is patent on *Figure 17* and results are given in *Table 11*.

Tab. 11: Results of analysis of chloride

Sample	Absorbance	Concentration [mg/l]
1	1.657	330.69
2	1.060	217.30
3	0.809	165.85
4	1.675	343.38
5	1.616	331.28
6	1.834	375.97
7	0.119	24.40
8	0.902	184.91
9	1.603	328.62
10	1.729	354.45

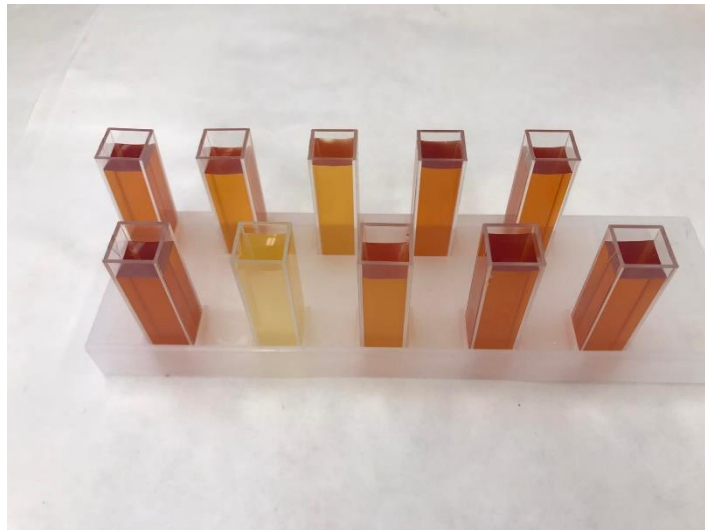


Fig. 17: Measuring solutions – back line from left: 1-5, front line from left: 6-10

3.4.6 Discussion of results

Obvious from *Table 12* the highest was concentration of sulfates followed by chlorides. Sulfates and chlorides are the most dangerous of ions together with nitrates. Concentration of nitrates was the third highest. This result was expected according to the bad condition of renders. The renders were taken from building, which displayed high intensity of moisture. Concentration of nitrites was the lowest. Determination of ammonium was not valid because of calcium cations from lime-based renders interfered with the measurement.

Tab. 12: Concentration of ions

Sample	SO ₄ ²⁻ [mg/l]	NH ₄ ⁺ [mg/l]	NO ₂ ⁻ [mg/l]	NO ₃ ⁻ [mg/l]	Cl ⁻ [mg/l]
1	372.30	7.06	16.98	85.04	330.69
2	536.06	2.92	0.37	3.66	217.30
3	522.26	0.34	0.29	4.01	165.85
4	429.06	1.34	0.18	4.59	343.38
5	550.12	1.76	0.55	3.48	331.28
6	502.21	1.81	30.55	1320.57	375.97
7	42.96	7.06	0.01	0.43	24.40
8	584.48	3.76	2.00	94.75	184.91
9	559.23	7.06	3.19	8.50	328.62
10	533.72	4.21	0.47	1.51	354.45

**Invalid values*

4 Conclusion

In the experimental part, five different methods of spectroscopic analysis on eluates of lime-based renders were performed. Determined ions were chosen based on their presumed incidence in analysed renders and their negative impact. Sulfates together with chlorides and nitrates are the most dangerous ions for building materials. For determination of sulfates, it was used turbidimetric method based on the resulting turbidity of solution. Chlorides were determined by thiocyanate method and nitrates by hydrazine method, which presents the sum of nitrates and nitrites. The nitrite value, obtained by the fourth method, was subtracted from the sum to get the concentration of nitrates. Concentration of these three dangerous ions was highest as expected. Renders were in very bad condition and objects, where they were taken, displayed high intensity of moisture and damage. The last method was determination of ammonium. The calcium content in lime-based renders strongly affected the measurement, therefore this method of determination of ammonium is not suitable for lime-based building materials.

Processes of analysis were similar for all five ions. Starting with weighting the chemicals and preparing reagents. Then analysis of a blank and six diluted solutions for calibration was made, followed by analysis of eluates. For determination of sulfates, 2 reagents were prepared, the preparation took at least 3 hours and analysis of one solution lasted only for 4 minutes. For determination of ammonium, 3 reagents were prepared. The preparation was very simple and took the least time of all five methods. Analysis lasted 8 minutes. For determination of chloride, 4 reagents were prepared. The preparation was the most demanding because it took 4 hours and 45 minutes at least, analysis itself went on for 7 minutes. For determination of nitrite, 2 reagents were needed. The preparation took 1 hour and 45 minutes in minimum and analysis of solution lasted for 6 minutes. For determination of sum of nitrite and nitrate, 3 solutions and 3 reagents were prepared. The preparation lasted for at least 2 hours and 45 minutes and analysis went on for 15 minutes. This determination was the most challenging.

Based on the results obtained in this UV/VIS spectrophotometric analysis is possible to evaluate its effectiveness and suitability. Once the calibration curve is constructed, measurement of solutions takes only minutes. There is possibility to measure more samples at once because spectrophotometric analysis itself takes a few seconds. Operation with the spectrophotometer is simple and intuitive. Even the most demanding preparation can be done in one day or more precisely within 6 hours. As for the disadvantages, some of the reagents are stable only for one week, for example sodium nitroprusside reagent and DIC reagent for

determination of ammonium and reduction reagent for determination of sum of nitrite and nitrate, which is stable for two weeks. Furthermore, some of the chemicals can be quite expensive, for example chemicals for determination of chlorides such as iron nitrate.

Determination of salt concentration in building materials using UV/VIS spectrophotometric analysis is the most suitable for measurement of larger number of samples at once, that means within the expiration date of the reagents. From this point of view the most suitable methods are determination of sulfates and chlorides, their reagents are stable for 3 months. This analysis is not appropriate for determination of ammonium in lime-based building materials. It is very disadvantageous to analyse low number of solutions as from the economic point of view and time demanding process. In conclusion the most effective in every aspect is determination of sulfates, followed by sum of nitrites and nitrates and determination of nitrites. Spectrophotometry is also suitable for determination of chlorides. Since the knowledge of salts concentration in building materials is crucial for their renovation, and chlorides, sulfates and nitrates are the most dangerous ions, UV/VIS spectrophotometry can be effectively used as a method of their determination.

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