VILNIUS UNIVERSITY
CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY
INSTITUTE OF CHEMISTRY

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# INVESTIGATION OF HISTORICAL ANALOGUES AND SOL-GEL PREPARATION OF NOVEL INORGANIC COBALT-BASED PIGMENTS

**Summary of doctoral dissertation**

Physical sciences, Chemistry - 03 P

Vilnius, 2011

The work was carried out in Vilnius University in the period 2006–2010.

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The summary of doctoral dissertation was mailed on the 20 of December 2010.

The dissertation is available at the Library of Vilnius University and at the Library of Institute of Chemistry.

VILNIAUS UNIVERSITETAS

FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRO CHEMIJOS INSTITUTAS

Dalia Jonynaitė

# KOBALTO NEORGANINIŲ PIGMENTŲ ISTORINIŲ ANALOGŲ TYRIMAS IR NAUJŲ SINTEZĖ ZOLIŲ-GELIŲ METODU

**Daktaro disertacijos santrauka**

Fiziniai mokslai, chemija - 03 P

Vilnius, 2011

Disertacija rengta 2006–2010 metais Vilniaus universitete.

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Disertacija bus ginama viešame Chemijos mokslo krypties tarybos posėdyje 2011 m. sausio 21 d. 14 val. Vilniaus universiteto Chemijos fakulteto Neorganinės chemijos auditorijoje. Adresas: Naugarduko 24, LT-03225 Vilnius, Lietuva. Tel.: 2193108. Faksas: 2330987.

Disertacijos santrauka išsiuntinėta 2010 m. gruodžio 20 d.

Disertaciją galima peržiūrėti Vilniaus universiteto ir FTMC Chemijos instituto bibliotekose.

# 1. INTRODUCTION

Cobalt-based ceramic pigments are widely used for coloured glazes in the ceramic industry for floor or wall whitewares, and also in the bulk coloration of polished, unglazed, porcelainized stoneware. They are characterized by having a high resistance with respect to light, environment, high temperature and chemicals. These pigments are also used in many industries because of their different colour, fine particle size, good hiding power, acid acceptance and compatibility with many organic and inorganic systems. The pallete of their colours is very large: blue, green, yellow, violet, brown and black. Recently new cobalt-based ceramic pigments have been synthesized using different synthetic approaches: sol-gel technology, traditional solid state reaction method, solution combustion method, microemulsion method, polymeric precursor method, chemical coprecipitation method.

There is a wide range of various historical cobalt pigments. Some of them were more important in the history of painting, others were more often used for decorating ceramic works or producing ceramic glaze. For example, cobalt yellow (Aureolin, $K_3[Co(NO_2)_6]$) has appeared in trade as a pigment in 1860. In those years it was the only steady bright yellow glazing colour used in the colour assortment together with the Indian yellow. Because of the remarkable effect this pigment is perfectly suitable for various painting techniques: aquarelle, tempera and oil. Also, it is used in glass, porcelain painting, and enamel. The most important violet cobalt pigments are different phosphates: cobalt violet brilliant light ($CoNH_4PO_4 \cdot H_2O$) and cobalt violet dark ($Co_3(PO_4)_2$). These pigments have been known since the end of the 18th century. Cobalt cerulean blue ($CoO \cdot nSnO_2$) was discovered in 1789. This pigment was used in enamel art, porcelain painting and oil painting. Cobalt blue dark and cobalt blue light ($CoO \cdot Al_2O_3$) pigments were already used in ancient Egypt for decorating pottery. Cobalt blue greenish ($Cr_2O_3 \cdot CoO \cdot Al_2O_3$) was produced in the middle of 19th century and used for the decorating porcelain. The colour of pigment varies from bluish green to greenish blue depending on the molar ratio of aluminium and chromium. Cobalt green bluish ($CoO \cdot ZnO$) was synthesized in 1778 and became more widely used in the 19th century. The pigment is resistant to light and suitable for all painting techniques. The blue cobalt pigment smalt ($CoO \cdot nSiO_2$) has also significant importance in art history. It was known and used as a pigment already in the 16th century,  but in the 17th century the smalt became one of the basic blue pigments in baroque style painting.

Owing to such wide applications of cobalt-based pigments, the characterization techniques of historical cobalt pigments in different mixtures are highly desirable. Moreover, the preparation of new cobalt-based ceramic pigments with different colour is very important task for materials research, conservation and restoration chemistry. In this study we report results of a systematic study of main historical cobalt-based pigments. The novel pigments were synthesized using environmentally benign sol–gel chemistry approach. Over the last few decades, the sol-gel techniques have been used to prepare a variety of mixed-metal oxides, nanomaterials and nanoscale architectures, nanoporous oxides, organic-inorganic hybrids. The results illustrate the influence of starting material, complexing agent, annealing temperature, heating time and other parameters on the phase purity and crystallinity of the end products.

**The main aim of this work was** to investigate the main cobalt-based pigments historical analogues and to synthesize and characterize novel cobalt-based pigments. For this reason there were formulated tasks as follows:

1. Investigation and systematic characterization of cobalt-based pigments historical analogues, their mixtures and glazes.
2. Synthesis and investigation of cobalt light violet $CoNH_4PO_4$ and comparison it's properties with commercial one from Kremer Pigmente.
3. Development of new FTIR spectroscopic analysis method for the determination of silica in the blue cobalt pigment smalt ($CoO{\cdot}nSiO_2$).
4. Sol-gel synthesis and characterization of novel cobalt-based pigments having spinel crystal structure: cobal aluminate, cobalt chromate and neodymium substituted cobalt aluminates ($CoAl_{1.75}Nd_{0.25}O_4$, $CoAl_{1.5}Nd_{0.5}O_4$, $CoAlNdO_4$).
5. Sol-gel synthesis and characterization of novel cobalt-based pigments having perovskite crystal structure: mixed neodymium and neodymium-yttrium cobaltates and cobaltates-aluminates.
6. Investigation of sol-gel chemistry approach to the preparation of perovskite erbium cobaltate.

**Statements for defence:**

1) Cobalt-based pigments historical analogues, their mixtures and glazes could be effectively characterized using X-ray diffraction analysis and FTIR spectroscopy method.
2) Coprecipitation synthesis method is suitable for the preparation of monophasic cobalt light violet $CoNH_4PO_4$ which properties are similar to the commercial one from Kremer Pigmente.
3) For the first time, it was demonstrated that FTIR spectroscopy could be effectively used for the determination of silica in the blue cobalt pigment smalt ($CoO \cdot nSiO_2$).
4) For the preparation of novel cobalt-based pigments $CoAl_{1.75}Nd_{0.25}O_4$, $CoAl_{1.5}Nd_{0.5}O_4$, $CoAlNdO_4$, $NdCoO_3$, $NdCo_{0.75}Al_{0.25}O_3$, $NdCo_{0.5}Al_{0.5}O_3$, $NdCo_{0.25}Al_{0.75}O_3$, $(Nd_{0.5}Y_{0.5})CoO_3$, $(Nd_{0.5}Y_{0.5})Co_{0.75}Al_{0.25}O_3$, $(Nd_{0.5}Y_{0.5})Co_{0.5}Al_{0.5}O_3$, $(Nd_{0.5}Y_{0.5})Co_{0.25}Al_{0.75}O_3$ the sol-gel method could be successfully used. However, the sol-gel synthesis of perovskite erbium cobaltate at the same synthesis conditions does not proceed.

## 2. EXPERIMENTAL

### *2.1 Materials and reagents*

Ten analytical grade individual pigments (Kremer Pigmente) were used for the characterization: $K_3[Co(NO_2)_6] \cdot 3H_2O$ (cobalt yellow, Aureolin), $CoNH_4PO_4 \cdot H_2O$ (cobalt violet brilliant light), $Co_3(PO_4)_2$ (cobalt violet dark), $CoO \cdot nSnO_2$ (cobalt cerulean blue), $CoO \cdot Al_2O_3$ (cobalt blue dark), $CoO \cdot Al_2O_3$ (cobalt blue light), $Cr_2O_3 \cdot CoO \cdot Al_2O_3$ (cobalt blue greenish), $CoO \cdot ZnO$ (cobalt green bluish), $CoO \cdot nSiO_2$ (smalt with different grind: 120 μm and 80 μm). The same pigments along with lead oxide ($Pb_3O_4$) and silica ($SiO_2$) were used for the preparation of cobalt-based glazes. For the preparation of cobalt light violet pigment analytical grade $CoCO_3$, $(NH_4)_3PO_4$ and $H_3PO_4$ were used as starting materials. For the interpretation, the properties of synthesized $CoNH_4PO_4 \cdot H_2O$ sample were compared with those of the commercial available cobalt light violet pigment (Kremer Pigmente). For the sol-gel synthesis of $CoAl_2O_4$, $CoCr_2O_4$, $CoAl_{1.75}Nd_{0.25}O_4$, $CoAl_{1.5}Nd_{0.5}O_4$ and $CoAlNdO_4$ stoichiometric amounts of $Al(NO_3)_3 \cdot 9H_2O$**,** $Cr(NO_3)_3 \cdot 9H_2O$**,** $Co(NO_3)_2 \cdot 6H_2O$ and $Nd_2O_3$ were used. For the sol-gel synthesis of

$NdCoO_3$, $NdCo_{0.75}Al_{0.25}O_3$, $NdCo_{0.5}Al_{0.5}O_3$, $NdCo_{0.25}Al_{0.75}O_3$, $(Nd_{0.5}Y_{0.5})CoO_3$, $(Nd_{0.5}Y_{0.5})Co_{0.75}Al_{0.25}O_3$, $(Nd_{0.5}Y_{0.5})Co_{0.5}Al_{0.5}O_3$, $(Nd_{0.5}Y_{0.5})Co_{0.25}Al_{0.75}O_3$ and $ErCoO_3$ stoichiometric amounts of $Co(NO_3)_2{\cdot}6H_2O$, $Co(CH_3COO)_2{\cdot}4H_2O$, $Al(NO_3)_3{\cdot}9H_2O$**,** $Y_2O_3$, $Nd_2O_3$ and $Er_2O_3$ were used. 1.2-ethanediol, tartaric acid and citric acid as complexing agents, all of them analytical grade, were used. For the preparation different solutions the initials salts or oxides were dissolved in 0.2 mol/l acetic acid or distilled water.

### *2.2 Methods of synthesis*

The cobalt-based pigments along with lead oxide ($Pb_3O_4$) and silica ($SiO_2$) were used for the preparation of cobalt-based glazes. In all cases the same molar ratio of ingredients has been selected $Pb_3O_4 : SiO_2 : \text{pigment} = 2.85 : 1.9 : 0.25$. The glazes were formed on the surface of terracotta (3x2 cm). The pigments were mixed with small amount of distilled water and pasted on the terracotta plate and dried for 10 h at room temperature. The glazes were annealed at 1000 $^{o}$C for 2.5 h.

For the preparation of cobalt light violet pigment $CoNH_4PO_4{\cdot}H_2O$, firstly 2.38 g of $CoCO_3$ was dissolved in 40 ml of 0.5 M $H_3PO_4$ at 65 $^{o}$C. Secondly, to the above solution 5 g of $(NH_4)_3PO_4$ dissolved in a small amount of distilled water was added. The obtained dark violet turbid solution was stirred for 1 h at the same temperature. Finally, the mixture was rapidly cooled within the ice bath. The obtained light violet powders were dried at room temperature. The yield of the reaction product was calculated to be nearly 98 %.

The anhydrous $SiO_2$ was obtained after annealing $SiO_2{\cdot}nH_2O$ at 950 $^{o}$C for 6 h in air using a heating rate of 5 $^{o}$C/min. The CoO was obtained by heating $Co(NO_3)_2{\cdot}6H_2O$ at 700 $^{o}$C for 5 h. The resulted mixture of cobalt oxides was additionally heated after intermediate grinding in an agate mortar at 930 $^{o}$C for 10 h. For the preparation of physical mixtures of CoO and $SiO_2$, the oxides were mixed at different molar ratios maintaining the amount of CoO constant and changing the amount of silica ($CoO:SiO_2$ = 1:1, 1:0.75, 1:0.5, 1:0.25, 1:0.1). For the preparation of pigment smalt $CoO{\cdot}nSiO_2$, the appropriate physical mixtures of oxides were heated for 5h in the range of 850-1000 $^{o}$C using a heating rate of 5 $^{o}$C/min.

For the preparation of nonsubstituted $CoAl_2O_4$ and $CoCr_2O_4$ samples, $Al(NO_3)_3{\cdot}9H_2O$**,** or $Cr(NO_3)_3{\cdot}9H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ were first dissolved in small amount of distilled water at 55-60 °C. To this solution, 2 ml of 1.2-ethanediol was added and the resulting mixture was stirred for 1 h at the same temperature. For the preparation of Nd- or Y–substituted samples firstly the appropriate amount of neodymium or yttrium oxide was dissolved in 50 mL of 0.2 mol/L $CH_3COOH$ at 65 °C. After stirring for 2 h the metal nitrates were added and the resulting mixtures were stirred for 1 h at the same temperature. The obtained violet, or blue, or black precursor gels were dried at 105 °C for 10 h. The oven dried gel powders were ground in an agate mortar and preheated for 3 h at 700 °C in air. After an intermediate grinding in an agate mortar, the powders were additionally sintered in air for 10 h at 1000 °C.

The same sol-gel chemistry approach was used for the preparation of $ErCoO_3$. In the sol-gel processing several complexing agents were tested (1.2-ethanediol, tartaric acid and citric acid).

### 2.3 Characterization techniques

The infrared spectra in the range of 4000–400 $cm^{-1}$ were recorded on Perkin-Elmer FT-IR Spectrum BX II FTIR spectrometer. Samples were prepared as KBr pellets (1.5%). Powder X-ray diffraction (XRD) measurements were performed at room temperature on DS Bruker AXS and Siemens D-500 diffractometers ($CuK_\alpha$ radiation: $\lambda$=1.5418 Å). Scanning electron microscopy (SEM) was used to study the morphology of the samples. The SEM analysis was performed under vacuum in the specimen chamber of scanning electron microscopes EVO 50 XVP and CamScan with EDX detecting system PV 7723 28 ME CamScan S-3000. Atomic force microscope (AFM) Veeco Bioscop II was also used for the characterization of synthesized glazes. The transmission spectra were recorded with SF-56 ir Perkin Elmer Lambda 35 UV VIS spectrophotometers. The optical Leitz microscope and digital camera Canon EOS 300 D were used for the surface characterization of the obtained glazes.

## 3. RESULTS AND DISCUSSION

### 3.1 Investigation and characterization of cobalt pigments historical analogues and their lead-based glazes

Ten individual historical pigments (Kremer Pigmente) were used for the characterization. The lead-based glazes obtained using all ten cobalt historical pigments showed very high quality.

### *3.1.1 XRD characterization of pigments and glazes*

In the present part, attention has been focused on the characterization of cobalt-based pigments and glazes using X-ray diffraction analysis. The identification of pigments in their mixtures or on unknown ceramic samples is very important not only for the characterization of materials, but also for non-destructive conservation and successful restoration, dating and authentication.

The X-ray diffraction pattern of cobalt yellow (Aureolin) pigment is shown in Fig. 1.

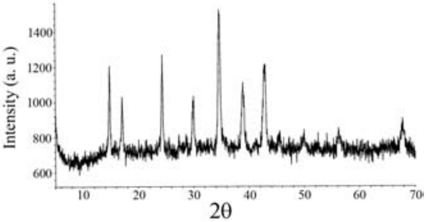

**Fig. 1.** X-ray diffraction pattern of cobalt yellow (Aureolin) pigment.

All diffraction peaks corresponds to standard diffractogram of $K_3[Co(NO_2)_6]$ (PDF [9-404]). The XRD pattern of cobalt yellow based glaze is shown in Fig. 2. Most of the diffraction lines seen in Fig. 2 could be attributed to the $Pb_3O_4$ phase (PDF [41-1493]). Besides, the most intensive line from silica at $2\theta \approx 20.8^{o}$ (PDF [34-717]) is also seen. However, no signals from cobalt yellow (Aureolin) pigment likely at $2\theta \approx 34.6^{o}$, $24.5\ ^{o}$ and $42.8^{o}$ could be detected in the XRD pattern of cobalt yellow based glaze.

The X-ray diffraction pattern of cobalt violet brilliant light pigment is typical XRD pattern of $CoNH_4PO_4{\cdot}H_2O$ (Fig. 3) (PDF [21-793]). The XRD pattern of cobalt violet brilliant light based glaze is shown in Fig. 4. The main diffraction peak of cobalt violet brilliant light pigment located at $2\theta \approx 10.0\ ^{o}$ apparently is seen in Fig. 4. Therefore we can conclude that contrary to the Aureolin, the cobalt violet brilliant light pigment could be distinguished in it's glaze by X-ray diffraction.

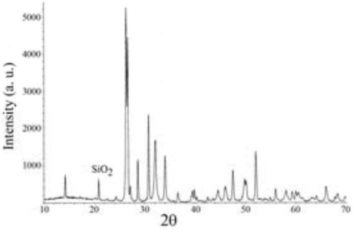

**Fig. 2.** X-ray diffraction pattern of cobalt yellow based glaze.

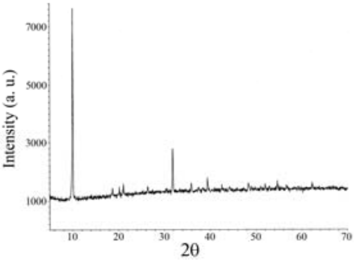

**Fig. 3.** X-ray diffraction pattern of cobalt violet brilliant light pigment.

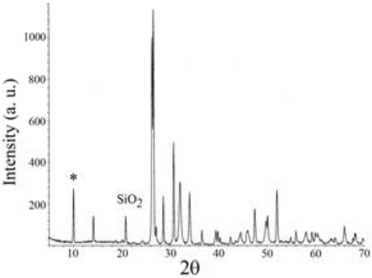

**Fig. 4.** X-ray diffraction pattern of cobalt violet brilliant light based glaze. (*) – $CoNH_4PO_4{\cdot}H_2O$.

The XRD pattern of cobalt violet dark pigment matches very well with XRD pattern of $Co_3(PO_4)_2$ (PDF [13-503]). However, to detect cobalt violet dark pigment in glaze using X-ray diffraction technique almost impossible. The formula cobalt cerulean blue pigment presented in the catalogue of Kremer Pigmente is given as $CoO{\cdot}nSnO_2$. However, the X-ray analysis data confirmed that the purchased reagent contains cobalt stannate spinel $Co_2SnO_4$ (PDF [29-514]) as a main phase and metal oxides $Co_3O_4$ (PDF [42-1467]) and $SnO_2$ (PDF [41-1445]) as secondary phases. The XRD results let us to conclude that cobalt cerulean blue pigment could be easily determined in glaze by XRD. Both, cobalt blue dark and cobalt blue light pigments in the Kremer Pigmente catalogue are described as $CoO{\cdot}Al_2O_3$ material. However the XRD patterns of these two pigments are quite different (see Figs. 5 and 6, respectively).

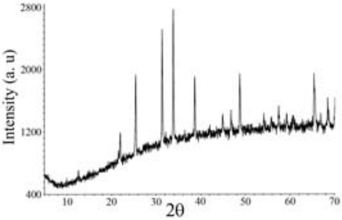

**Fig. 5.** X-ray diffraction pattern of cobalt blue dark pigment.

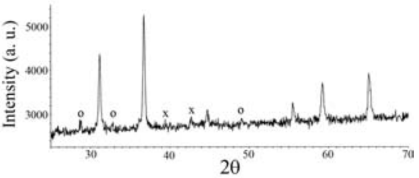

**Fig. 6.** X-ray diffraction pattern of cobalt blue light pigment. (o) – $Al_2O_3$ and (x) – CoO.

Surprisingly, the XRD pattern of cobalt blue dark pigment (Fig. 5) does not contain any reflections from known inorganic phases of cobalt and aluminium. Therefore, the phase composition of this pigment was not identified. On the other hand, the X-ray analysis data of cobalt blue light pigment (Fig. 6) confirmed that the purchased reagent contains cobalt aluminate spinel $CoAl_2O_4$ (PDF [38-814]) as a main phase and metal oxides $Al_2O_3$ (PDF [35-1121]) and CoO (PDF [9-402]) as secondary phases. According to the XRD patterns of cobalt blue based glazes, the cobalt blue pigments, especially cobalt blue light pigment, could be detected by XRD in their glazes.

According to the XRD results, the cobalt blue greenish pigment is cobalt chromate spinel $CoCr_2O_4$ (PDF [22-1084]), but not mixture of separate oxides $Cr_2O_3 \cdot CoO \cdot Al_2O_3$. Moreover, the phases containing aluminium have not been determined. It is possible that alumina exists as separate amorphous phase. Unfortunately, no even traces of $CoCr_2O_4$ could be detected in the glaze using XRD technique. The XRD pattern of cobalt green bluish pigment corresponds the XRD pattern of ZnO (PDF [36-1451]) as a main phase along with diffraction lines from CoO (PDF [43-1004]) phase. These results are in a good agreement with a nominal composition of pigment ($CoO \cdot ZnO$). The XRD results suggest that contrary to the cobalt blue greenish pigment, the cobalt green bluish pigment could be distinguished in it's glaze by X-ray diffraction. Finally, Fig. 7

represents two XRD patterns of smalt pigment ($CoO \cdot nSiO_2$) having different particle size 120 μm and 80 μm.

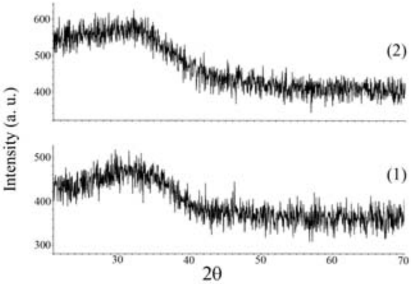

**Fig. 7.** X-ray diffraction pattern of cobalt smalt pigments having different particle size: (1) –120 μm and (2) – 80 μm.

As seen, both XRD patterns show only amorphous character and no any crystalline phases could be identified. Therefore, the further experiment with smalt based glazes was not proceed.

### *3.1.2 FTIR characterization of pigments and glazes*

This part presents the results of characterization historical cobalt pigments and glazes using FTIR spectroscopy. Fig. 8 represents IR spectra of cobalt yellow ($[K_3(Co(NO_2)_6] \cdot 3H_2O$, Aureolin) pigment and glaze. In the spectrum of aureolin the peaks 1396 $cm^{-1}$, 1333 $cm^{-1}$, 832 $cm^{-1}$, 633 $cm^{-1}$ ir 413 $cm^{-1}$ correspond to N-O vibrations. Also, O-H stretching and bending vibrations could be detectible at 4000-3000 $cm^{-1}$ and 1651 $cm^{-1}$, respectively. Moreover, some of these absorption lines are seen in the IR spectrum of glaze (marked with asterisk). So, we can conclude that IR spectroscopy could be used for the characterization of cobalt yellow in it's glazes.

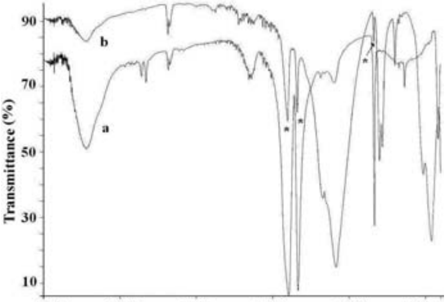

**Fig. 8.** IR spectra of Aureolin (a) and it's glaze (b).

Both, cobalt violet light and cobalt violet dark pigments could be also determined in their glazes using IR spectroscopy. The IR spectra of cobalt cerulean and it's glaze are shown in Fig. 9.

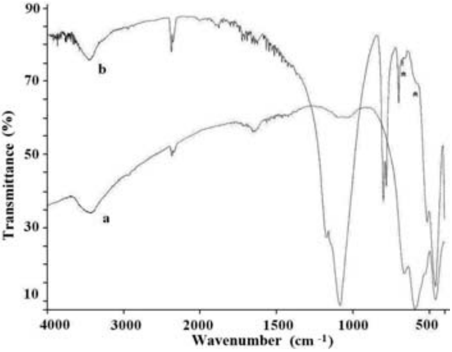

**Fig. 9.** IR spectra of cobalt cerulean (a) and it's glaze (b).

Apparently, that identification of cerulean in it's glaze using IR spectrum presented in Fig. 9 is problematic. Generally, these investigations let us to conclude that IR spectroscopy is indispensable tool for the characterization of non-oxide historical cobalt pigments in their glazes. However, the IR spectra of oxides contain absorption lines which overlapping with similar absorptions generated by other constituents of historical cobalt glazes.

### *3.1.3 SEM characterization of pigments and glazes*

The glazes obtained from historical cobalt pigments were characterized by scanning electron microscopy. Interestingly, the morphology of all glazes is very similar independent on the cobalt pigment used for the preparation of glaze. For example, the SEM images of cobalt blue dark and cobalt blue greenish glazes are shown in Figs. 10 and 11, respectively.

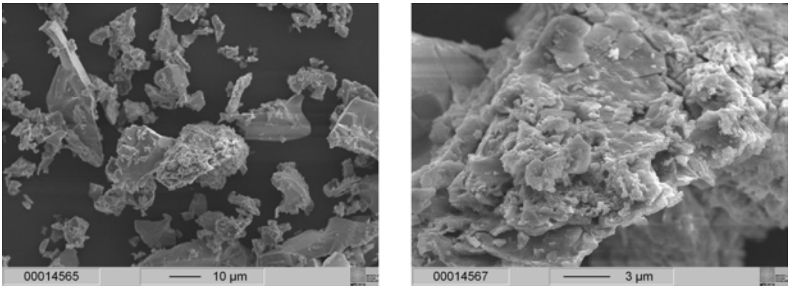

**Fig. 10.** SEM micrographs of cobalt blue dark glaze at different magnification.

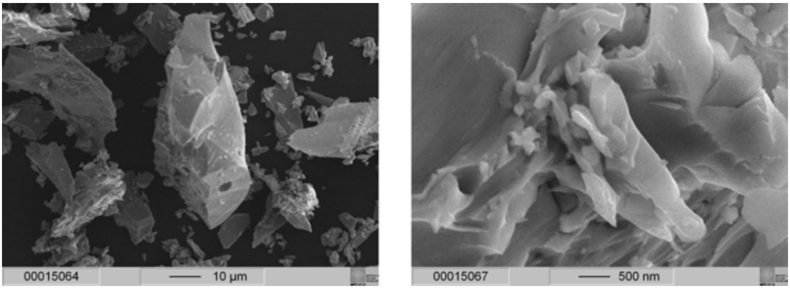

**Fig. 11.** SEM micrographs of cobalt blue greenish glaze at different magnification.

The solids consist of different size (from 100 nm to 10 μm) plate-like crystallites. The surface of glazes is not smooth enough, the larger crystals are covered with smaller particles. The similarity of all SEM images let us to conclude that the main morphological features of glazes are not dependent on the nature of cobalt pigment. The surface morphology is determined by other constituents of glazes, such as led oxide, silica or terracotta.

### 3.2 Synthesis and characterization of cobalt violet light pigment $CoNH_4PO_4$

The purpose of the present work was to prepare and characterize cobalt light violet pigment ($CoNH_4PO_4 \cdot H_2O$) by a simple co-precipitation method. The X-ray diffraction patterns of the synthesized, purchased from Kremer Pigmente pigment samples and standard XRD pattern of ammonium cobalt phosphate hydrate (PDF [21-793]) were almost identical. Therefore, we can conclude from XRD data that the single phase cobalt light violet pigment has been synthesized using a simple co-precipitation approach. These results are almost consistent with those observed by the IR measurements. The IR spectra of both samples are qualitatively identical regardless their preparation history. The IR spectra of the synthesized and obtained from Kremer Pigmente pigment samples are presented in Fig. 12.

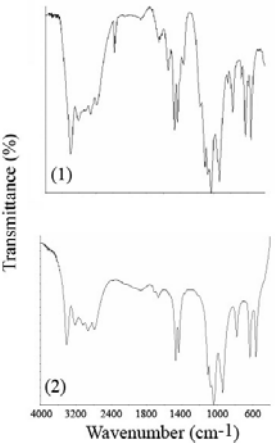

**Fig. 12.** IR spectra recorded for $CoNH_4PO_4{\cdot}H_2O$ pigment samples: synthesized (1), from Kremer Pigmente (2).

The distinctive feature observed in both spectra of the pigment samples is absorptions around 3400 $cm^{-1}$ (strong) and 1660 $cm^{-1}$ (weak) indicating the presence of water of crystallization. A number of strong and multiple absorptions in the range of 3220-2775 $cm^{-1}$ and at 1469, 1431, 781 $cm^{-1}$ could be attributed to the characteristic vibrations in $NH_4^+$. The absorption bands attributable to the characteristic P-O vibrations in phosphate are clearly seen at 1103-937 $cm^{-1}$ and 625-561 $cm^{-1}$. The optical properties for the both $CoNH_4PO_4{\cdot}H_2O$ samples were also recorded. The optical reflection spectra were measured at room temperature in the range of 400–700 nm. The reflection spectra qualitatively were almost identical. In the beginning the pigment samples show a wavelength independent reflectance (from 400 nm up to ~445 nm, and up to ~430 nm for synthesized and Kremer Pigmente samples, respectively). From this point a significant increase of reflection up to ~525 nm is seen. Starting from ~525 nm the reflection abruptly decreases and again increases starting from ~555 nm. In the higher wavelength region (from ~650 nm) the reflection is almost constant, i.e. not wavelength dependent, and close to unity, which proves the high optical quality of the samples.

It is interesting to note that almost identical surface microstructure and particle size were observed for both pigment samples (Figs. 13 and 14).

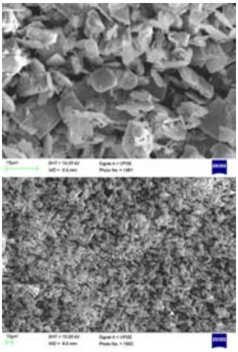

**Fig. 13.** SEM micrographs of the synthesized by co-precipitation $CoNH_4PO_4 \cdot H_2O$ pigment obtained at two magnifications.

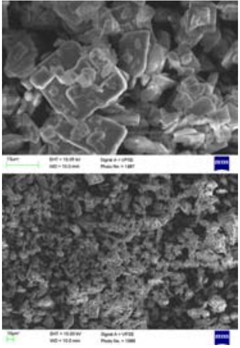

**Fig. 14.** SEM micrographs of the $CoNH_4PO_4 \cdot H_2O$ pigment from Kremer Pigmente obtained at two magnifications.

In both cases the plate-like particles are seen with very well pronounced agglomeration, indicating a good connectivity between the grains. Moreover, it was clear that micrograin network was also formed. The SEM micrograph suggests that the $CoNH_4PO_4 \cdot H_2O$ solids synthesized by co-precipitation route are composed of irregular submicron grains with an average grain size of less than 5 μm. In the case of $CoNH_4PO_4 \cdot H_2O$ sample purchased from Kremer Pigmente, the formation of plate-like ultrafine crystallites with an average grain size of ~3-12 μm is evident. As seen, the adjacent grains tend to fuse and microscopic crystal growth on each grain begins to occur.

### 3.3 Synthesis and characterization of historical cobalt smalt pigment ($CoO \cdot nSiO_2$)

In this part the application of FTIR spectroscopic technique for the characterization of blue cobalt pigment smalt ($CoO \cdot nSiO_2$) is reported. A novel FTIR spectroscopic determination of silica in physical mixture of CoO and $SiO_2$ and in the cobalt pigment smalt $CoO·nSiO_2$ has been suggested.

### *3.3.1 Synthesis and characterization of $CoO·nSiO_2$ mixtures and cobalt smalt pigment*

As seen from Fig. 7, both XRD patterns of cobalt pigment smalt show only amorphous character and no any crystalline phases could be identified. Evidently, the XRD technique is not suitable for the characterization of this type pigments. Therefore, for further experiments only FTIR spectroscopy was used. The FTIR spectrum of CoO synthesized at 930 $^{o}$C is presented in Fig. 15. As seen, very intensive Co-O bands are found at 664 and 578 $cm^{-1}$.

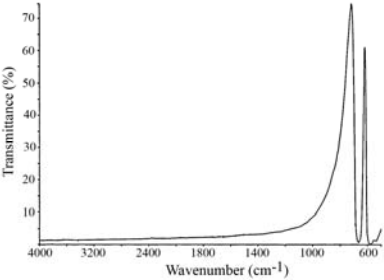

**Fig. 15.** FTIR spectra of CoO.

Fig. 16 represents the FTIR spectrum of silica. Several absorptions are observed in FTIR spectrum of $SiO_2$. Two bands located at 3434 $cm^{-1}$ and 1629 $cm^{-1}$ can be assigned to the adsorbed water during the exposure of dried powder to air. Si–O antisymmetric stretching band is found at 1108 $cm^{-1}$, Si–O symmetric stretching band at 804 $cm^{-1}$, and Si–O rocking motion band at approximately 500 $cm^{-1}$. According to the origin of the bands, it is clearly seen that main absorptions in the FTIR spectra of CoO and $SiO_2$ are located in different regions. Therefore, this feature could be useful for the identification of CoO and $SiO_2$ in blue cobalt pigment smalt by FTIR spectroscopy.

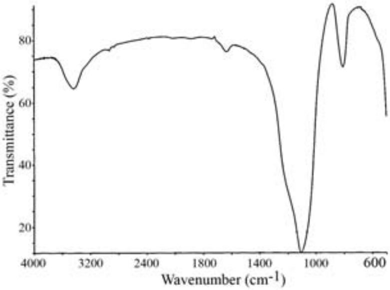

**Fig. 16.** FTIR spectra of $SiO_2$.

The FTIR spectra of physical mixtures of CoO and $SiO_2$ having the minimum and maximum molar fraction of silica showed that the location of characteristic peaks attributable to Co–O vibrations (664 and 578 $cm^{-1}$) is the same as in the spectrum of individual oxide. The position of Si–O antisymmetric stretching band remains steady (1105 $cm^{-1}$), however, the position of Si–O symmetric stretching band slightly moved from 804 $cm^{-1}$ for pure silica to 812 $cm^{-1}$ in the case of physical mixture of two oxides. Moreover, the intensities of Si–O structural bands apparently depend on the amount of silica in the mixture. So, by changing molar fraction of $SiO_2$ in the mixture the changes only in the region 1600-500 $cm^{-1}$ of FTIR absorption spectra could be expected.

Fig. 17 provides the FTIR spectra of physical mixtures of CoO and $SiO_2$ having different molar fraction of silica. The distinctive feature observed in these FTIR spectra is that intensity or integrated peak area of Si–O bands located at 812 $cm^{-1}$ increases with increasing amount of silica in the mixture of oxides. The FTIR absorption spectra in the region of 1600-500 $cm^{-1}$ for the $CoO \cdot nSiO_2$ products obtained at 850 $^{o}$C are shown in Fig. 18. Compared to Fig. 17 almost similar situation was observed. Evidently, the intensity or integrated peak area of Si–O bands located at 812 $cm^{-1}$ increases with increasing amount of silica up to 50 mol% in the blue cobalt smalt pigment synthesized at 850 $^{o}$C. Analogous FTIR results were obtained by synthesizing blue cobalt smalt pigments at 900 $^{o}$C.

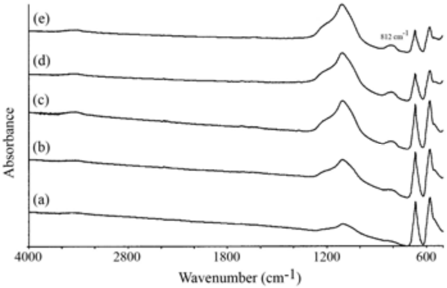

**Fig. 17.** FTIR spectra of physical mixtures of CoO and $SiO_2$ having different molar fraction of silica. n($SiO_2$): 9.1 mol% (a), 20 mol% (b), 33.3 mol% (c), 42.9 mol% (d) and 50 mol% (e).

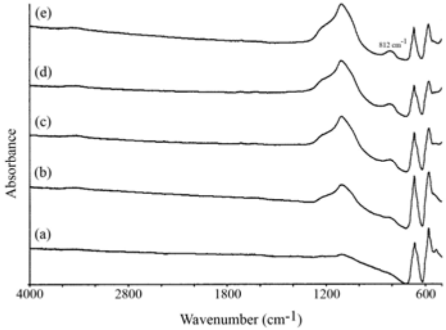

**Fig. 18.** FTIR spectra of CoO·n$SiO_2$ synthesized at 850 °C using different molar fraction of silica. n($SiO_2$): 9.1 mol% (a), 20 mol% (b), 33.3 mol% (c), 42.9 mol% (d) and 50 mol% (e).

### *3.3.2 IR spectroscopic determination of $SiO_2$ in smalt (CoO·n$SiO_2$)*

The dependence of integrated peak area of Si–O bands located at 812 $cm^{-1}$ on the molar ratio of CoO and $SiO_2$ in their mixtures is presented in Fig. 19. As seen, the calibration curve shows almost linear correlation within the molar fraction of 9.1 – 50 mol% of $SiO_2$. Such observation let us to show that FTIR spectroscopy could be successfully used for the determination of silica in the mixtures of CoO and $SiO_2$ when molar fraction of silica ranges in the 9.1 – 50 mol%. For the spectroscopic determination of $SiO_2$ in blue cobalt smalt pigments the FTIR results obtained for the CoO·n$SiO_2$ samples synthesized at 850 °C were used. The calibration curve showed almost linear correlation within the molar fraction of 20–50 mol% of $SiO_2$. The results for the determination of silica in the CoO·n$SiO_2$ samples purchased at Kremer Pigmente are shown in Table 1.

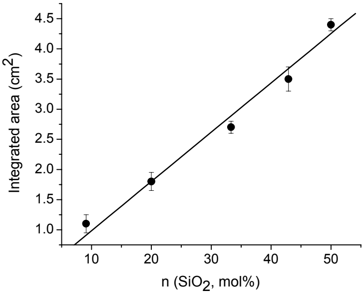

**Fig. 19.** The dependence of integrated peak area of Si–O bands located at 812 cm$^{-1}$ on the molar ratio of CoO and $SiO_2$ in their mixtures.

**Table 1.** FTIR results for the determination of $SiO_2$ in blue cobalt smalt pigments $CoO \cdot nSiO_2$. (n = 5).

| Sample | The integrated area of the Si-O band at 812 cm$^{-1}$ (cm$^2$) | Amount of $SiO_2$, mol % | Standard deviation $S_r$, % |
|---|---|---|---|
| 1 | 5.38 | 49.5 | 4.0 |
| 2 | 4.99 | 46.8 | 3.8 |

Thus, the exact chemical formulas of blue cobalt smalt pigments determined using FTIR data corresponds to $CoO \cdot 0.98SiO_2$ and $CoO \cdot 0.88SiO_2$ for the samples 1 and 2, respectively. Finally, the small values of standard deviations presented in Table 1 suggest that spectroscopic determination of silica in blue cobalt smalt pigments could be performed with sufficient accuracy.

### 3.4 Sol-gel synthesis and characterization of cobalt blue $CoAl_2O_4$ and novel cobalt pigments $CoCr_2O_4$, $CoAl_{1.75}Nd_{0.25}O_4$, $CoAl_{1.5}Nd_{0.5}O_4$, $CoAlNdO_4$

This part reports on the results concerning the sol-gel preparation of cobalt blue $CoAl_2O_4$ and novel cobalt pigments $CoCr_2O_4$, $CoAl_{1.75}Nd_{0.25}O_4$, $CoAl_{1.5}Nd_{0.5}O_4$, $CoAlNdO_4$. The metal ions, generated by dissolving starting materials of metals in the diluted acetic acid were complexed by 1.2-ethanediol to obtain the precursors for the ceramic materials. The XRD results clearly showed, that monophasic $CoAl_2O_4$ (PDF [44-160]) and $CoCr_2O_4$ (PDF [22-1084]) spinels have formed during sol-gel synthesis. The XRD patterns of $CoAl_{1.75}Nd_{0.25}O_4$, $CoAl_{1.5}Nd_{0.5}O_4$ and $CoAlNdO_4$ ceramics showed the formation of fully crystallized oxides with well pronounced spinel crystal structure. The XRD pattern of the representative $CoAlNdO_4$ sample is presented in Fig. 20. The XRD data confirm the formation of $CoAlNdO_4$ solid solution.

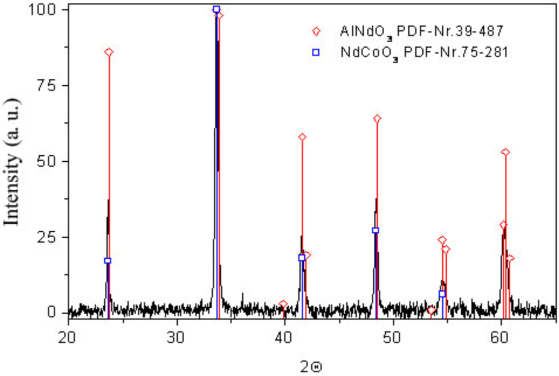

**Fig. 20.** X-ray diffraction pattern of $CoAlNdO_4$ sample prepared using sol-gel processing.

SEM investigation showed that sol-gel derived $CoCr_2O_4$ and $CoAl_2O_4$ are composed of rather large (~50µm) differently shaped crystallites. Slightly smaller particles have formed in the case of $CoAl_{1.75}Nd_{0.25}O_4$, $CoAl_{1.5}Nd_{0.5}O_4$ and $CoAlNdO_4$ ceramics. Besides, the intensity of pigments colour decreases with decreasing amount of aluminium in these mixed-metal compounds. The obtained glazes have very intensive and expressive colours. Besides, the colour of novel glazes containing $CoAl_{1.75}Nd_{0.25}O_4$, $CoAl_{1.5}Nd_{0.5}O_4$ and $CoAlNdO_4$ pigments could be easily controlled by molar ratio of aluminium and neodymium.

Fig. 21 shows the AFM images of synthesized glazes. The glaze with $CoCr_2O_4$ pigment contains different bumps in size of 20 µm. The roughness of glaze with $CoAl_2O_4$ is a bit smaller (~5-10 µm). Interestingly, the surfaces of glazes sintezed with neodymium substituted $CoAl_{1.75}Nd_{0.25}O_4$, $CoAl_{1.5}Nd_{0.5}O_4$ and $CoAlNdO_4$ pigments are sufficiently smooth.

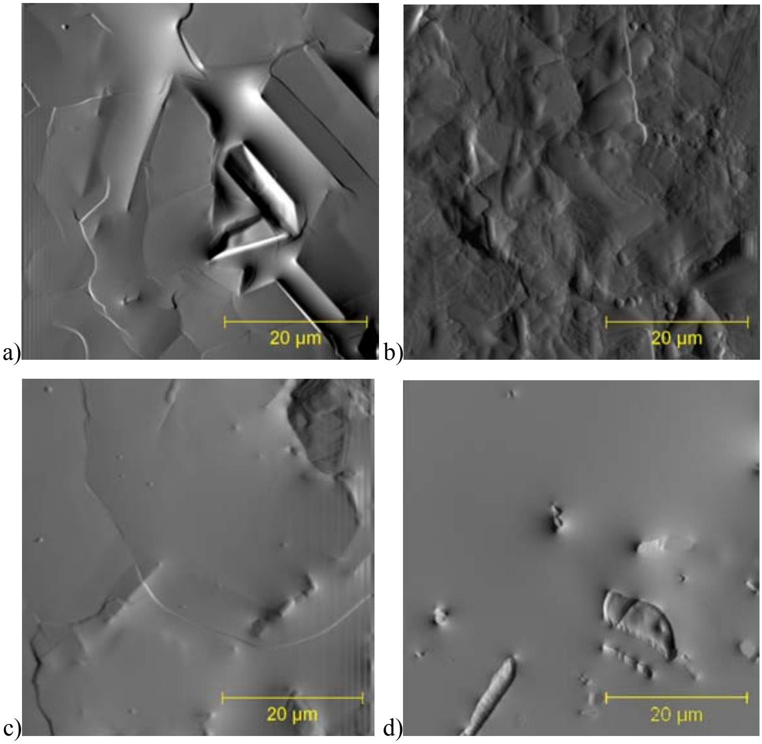

**Fig. 21.** AFM images of glazes with different sol-gel derived cobalt pigments: a) $CoCr_2O_4$, b) $CoAl_2O_4$, c) $CoAl_{1.75}Nd_{0.25}O_4$ ir d) $CoAlNdO_4$.

### 3.5 Sol-gel synthesis and characterization of novel cobalt pigments $NdCoO_3$, $NdCo_{0.75}Al_{0.25}O_3$, $NdCo_{0.5}Al_{0.5}O_3$, $NdCo_{0.25}Al_{0.75}O_3$ and $(Nd_{0.5}Y_{0.5})CoO_3$, $(Nd_{0.5}Y_{0.5})Co_{0.75}Al_{0.25}O_3$, $(Nd_{0.5}Y_{0.5})Co_{0.5}Al_{0.5}O_3$, $(Nd_{0.5}Y_{0.5})Co_{0.25}Al_{0.75}O_3$

This part presents on the results of sol-gel preparation of new cobalt-based pigments. In the perovskite cobalt aluminate $NdCoO_3$ neodymium was partially substituted by yttrium and cobalt by aluminium. The XRD patterns of the obtained ceramics are shown in Figs. 22 and 23. The XRD pattern of sol-gel synthesized $NdCoO_3$ fits completely with PDF data ([25-1064]). The most intensive lines are observed at $2\theta \approx 33.6^{\circ}$ (220) - 100%; $2\theta \approx 60.0^{\circ}$ (422) – 40 % and $2\theta \approx 48.2^{\circ}$ (400) - 35%.

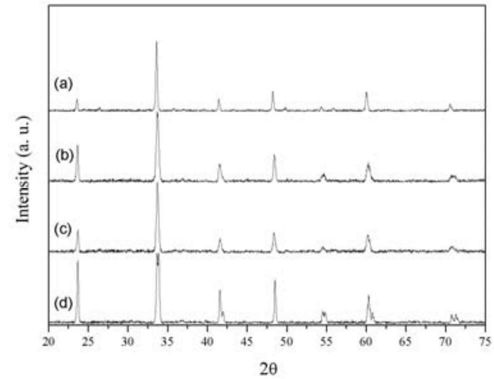

**Fig. 22.** X-ray diffraction patterns of $NdCoO_3$ (a), $NdCo_{0.75}Al_{0.25}O_3$ (b), $NdCo_{0.5}Al_{0.5}O_3$ (c), $NdCo_{0.25}Al_{0.75}O_3$ (d) samples prepared using sol-gel processing.

By substitution cobalt with aluminium the diffraction lines slightly moves to the smaller 2θ values. When aluminium amount reaches 75%, in the XRD pattern of $NdCo_{0.25}Al_{0.75}O_3$ the peaks attributable to the $NdAlO_3$ phase also could be detected. The XRD patterns of neodymium-yttrium cobaltate $(Nd_{0.5}Y_{0.5})CoO_3$ and neodymium-yttrium cobaltate-aluminates $(Nd_{0.5}Y_{0.5})Co_{0.75}Al_{0.25}O_3$, $(Nd_{0.5}Y_{0.5})Co_{0.5}Al_{0.5}O_3$, $(Nd_{0.5}Y_{0.5})Co_{0.25}Al_{0.75}O_3$ are shown in Fig. 23.

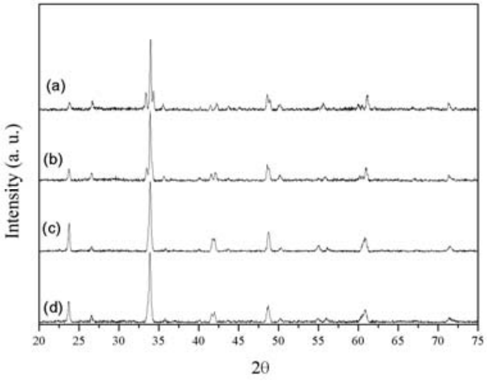

**Fig. 23.** X-ray diffraction patterns of $(Nd_{0.5}Y_{0.5})CoO_3$ (a), $(Nd_{0.5}Y_{0.5})Co_{0.75}Al_{0.25}O_3$ (b), $(Nd_{0.5}Y_{0.5})Co_{0.5}Al_{0.5}O_3$ (c), $(Nd_{0.5}Y_{0.5})Co_{0.25}Al_{0.75}O_3$ (d) samples prepared using sol-gel processing.

As seen from Fig. 23, the neodymium-yttrium cobaltate and neodymium-yttrium cobaltate-aluminates are monophasic perovskite structure compounds. There can not be seen any impurity phases.

The prepared glazes using these novel cobalt pigments showed bluish colour which intensity depends on the chemical composition of mixed-metal cobaltates. Therefore, we can conclude that these new materials could be successfully used as ceramic pigments.

### 3.6 Sol-gel synthesis and characterization of novel cobalt pigment $ErCoO_3$

The same sol-gel chemistry approach has been applied for the preparation of erbium cobaltate. To date, this compound has not been synthesized at ambient oxygen pressure. However, the XRD pattern of the obtained synthesis product showed formation only two separate oxides $Er_2O_3$ and $Co_3O_4$. Semiquantitative analysis also showed that the end product contains 78 % of $Er_2O_3$ and 22 % of $Co_3O_4$. Therefore, this material was not used for the preparation of cobalt glaze which expected to be a combination of two nice pink and blue colours. Thus, the development of simple synthesis route to $ErCoO_3$ still remains an interesting and important scientific task.

## CONCLUSIONS

1. XRD analyses clearly showed that chemical composition of some purchased (Kemer Pigmente) cobalt-based pigments (cobalt yellow, cobalt violet brilliant light, cobalt violet dark, cobalt green bluish) corresponds to the given in the Kremer Pigmente catalogue. However the chemical composition of several pigments has been slightly corrected. The cobalt cerulean blue pigment contains cobalt stannate spinel $Co_2SnO_4$ as a main phase and metal oxides $Co_3O_4$ and $SnO_2$ as secondary phases. The cobalt blue light pigment contains cobalt aluminate spinel $CoAl_2O_4$ as a main phase and metal oxides $Al_2O_3$ and CoO as secondary phases. According to the XRD results, the cobalt blue greenish pigment is cobalt chromate spinel $CoCr_2O_4$, but not mixture of separate oxides $Cr_2O_3 \cdot CoO \cdot Al_2O_3$. Besides, the XRD pattern of cobalt blue dark pigment does not contain any reflections from known inorganic phases of cobalt and aluminium. The cobalt smalt pigment ($CoO \cdot nSiO_2$) is completely amorphous material.

2. It was demonstrated that contrary to the cobalt yellow, cobalt violet dark, cobalt blue greenish and cobalt smalt, the cobalt violet brilliant light, cobalt cerulean blue, cobalt blue dark, cobalt blue light and cobalt green bluish pigments could be distinguished in the appropriate glazes by X-ray diffraction. Thus, the XRD analysis is significant analytical tool for the characterization of historical pigments and glazes.
3. The results of IR spectroscopic investigations clearly demonstrated that this method could be successfully used for the qualitative determination of non-oxide cobalt pigments aureoline $[K_3(Co(NO_2)_6]\cdot 3H_2O$, cobalt violet light $CoNH_4PO_4\cdot H_2O$, cobalt violet dark $Co_3(PO_4)_2$ in their lead-based glazes.
4. Cobalt light violet pigment ($CoNH_4PO_4\cdot H_2O$) has been prepared by a co-precipitation method. The characteristics of obtained synthesis product were compared with those for the commercial sample purchased at Kremer Pigmente.
5. For the first time to our knowledge, it was demonstrated that the characteristic Si-O absorption band at 812 $cm^{-1}$ could be successfully used as indicator in the evaluation of molar ratio of CoO and $SiO_2$ in their mixture. The integrated peak area linearly depends on the mole fraction of $SiO_2$ in the physical mixture of CoO and $SiO_2$ (in the range of 9.1-50 %), and in the cobalt pigment smalt synthesized at 850-900 $^{o}C$ (in the range of 20-50 %). A novel FTIR spectroscopic determination of silica in physical mixture of CoO and $SiO_2$ or in the cobalt pigment smalt $CoO\cdot nSiO_2$ has been suggested.
6. New cobalt-based pigments having spinel crystal structure such as $CoAl_2O_4$, $CoCr_2O_4$ and similar systems in which aluminium was partially replaced by neodymium $CoAl_{1.75}Nd_{0.25}O_4$, $CoAl_{1.5}Nd_{0.5}O_4$, $CoAlNdO_4$ have been synthesized using an aqueous sol-gel chemistry technique. The obtained glazes showed sufficient colour characteristics.
7. For the first time, novel perovskite structure compounds $NdCoO_3$, substituted neodymium cobaltates-aluminates ($NdCo_{0.75}Al_{0.25}O_3$, $NdCo_{0.5}Al_{0.5}O_3$, $NdCo_{0.25}Al_{0.75}O_3$) and mixed neodymium-yttrium analogues $(Nd_{0.5}Y_{0.5})CoO_3$, $(Nd_{0.5}Y_{0.5})Co_{0.75}Al_{0.25}O_3$, $(Nd_{0.5}Y_{0.5})Co_{0.5}Al_{0.5}O_3$, $(Nd_{0.5}Y_{0.5})Co_{0.25}Al_{0.75}O_3$ have been synthesized by sol-gel synthesis method. The obtained glazes using these novel cobalt pigments showed bluish colour which intensity depends on the chemical composition of mixed-metal cobaltates.

8. It was demonstrated, that the same sol-gel chemistry approach can not be used for the preparation of erbium cobaltate. The XRD pattern of the obtained synthesis product showed formation only two separate oxides $Er_2O_3$ and $Co_3O_4$.
9. The similarity of all SEM images of cobalt-based glazes let us to conclude that the main morphological features of glazes are not dependent on the nature of cobalt pigment. The surface morphology is determined by other constituents of glazes, such as led oxide, silica or terracotta. Therefore, the SEM method is not very useful for the characterization of cobalt-based glazes.

## The List of Original Publications by the Author

### Articles in journals

1. D. Jonynaitė, D. Jasaitis, J. Senvaitienė, A. Kareiva, A. Selskis and R. Juškėnas. Synthesis of $CoNH_4PO_4$ pigment by co–precipitation method. *Chemija,* 19 (2008) 23-26.
2. D. Jonynaitė, J. Senvaitienė, J. Kiuberis, A. Kareiva, R. Juškėnas, R. Ramanauskas. XRD characterization of cobalt-based historical pigments and glazes. *Chemija,* 20 (2009) 10-18.
3. D. Jonynaite, J. Senvaitiene, A. Beganskiene, A. Kareiva. Spectroscopic analysis of blue cobalt smalt pigment. *Vibrational Spectroscopy,* 52 (2010) 158-162.

### Published contributions to academic conferences

1. D. Jonynaite, J. Smirnova, A. Buitvydas, A. Beganskiene, D. Jasaitis, J. Kiuberis, J. Senvaitiene and A. Kareiva. Characterization of cobalt-based pigments and glazes. 8th National Lithuanian Conference „Chemistry 2007“, Vilnius, Lithuania, October 12, (2007) 29.
2. D. Jonynaite, J. Senvaitiene, D. Jasaitis, A. Selskis, R. Juskenas and A. Kareiva. Synthesis and characterization of cobalt light violet pigment. 8th Conference on Solid State Chemistry. Bratislava, Slovak Republic, July 6-11, (2008) 219.
3. D. Jonynaite, D. Jasaitis, A. Buitvydas, A. Selskis, R. Juskenas and A. Kareiva. Synthesis of $CoNH_4PO_4$ pigment by co-precipitation method. Conference ”Chemistry

and Technology of Inorganic Compounds”. Kaunas, Lithuania, April 23, (2008) 15-16.

4. D. Jonynaite, J. Senvaitiene, A. Beganskiene and A. Kareiva. IR spectroscopic determination of silica in blue cobalt smalt pigment. 9th National Lithuanian Conference „Chemistry 2009“. Vilnius, Lithuania, October 16, (2009) 27.

## CURRICULUM VITAE

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1976-1981 Master Studies at Vilnius University - Master Degree in 1981 Biology.

2006–2010 Post-graduate studies at the Department of General and Inorganic Chemistry, Faculty of Chemistry of Vilnius University.

Since 1980 she has been working at the P. Gudynas Restoration Centre of Lithuanian Art Museum in different positions.

## KOBALTO NEORGANINIŲ PIGMENTŲ ISTORINIŲ ANALOGŲ TYRIMAS IR NAUJŲ SINTEZĖ ZOLIŲ-GELIŲ METODU

### SANTRAUKA

Kobalto pigmentų (Kemer Pigmente, Vokietija) Rentgeno spindulių difrakcinė analizė (XRD) parodė, kad kai kurių pigmentų cheminė sudėtis, nurodyta kataloguose, skiriasi nuo nustatytos: kobalto pigmentas ceruleumas yra $Co_2SnO_2$ (pagrindinė fazė), $SnO_2$ ir $Co_3O_4$ mišinys, o ne $CoO\cdot nSnO_2$; kobalto mėlynas šviesusis - $CoAl_2O_4$ (pagrindinė fazė), $Al_2O_3$ ir CoO mišinys, o ne $CoO\cdot Al_2O_3$; kobalto melsvai žalias $CoCr_2O_4$ (pagrindinė fazė), o ne $Cr_2O_3\cdot CoO\cdot Al_2O_3$; kobalto mėlynojo tamsiojo fazinė sudėtis neturi nieko bendro su $CoO\cdot Al_2O_3$. Atlikta istorinių kobalto pigmentų analogų Rentgeno spindulių difrakcinė analizė parodė, kad metodas efektyvus, nustatant kobalto šviesiai violetinį $CoNH_4PO_4\cdot H_2O$, kobalto mėlynąjį šviesų, ceruleumą ir kobalto žalsvai mėlyną $CoO\cdot ZnO$, jų švino glazūrose, bet netinka aureolino $[K_3(Co(NO_2)_6]\cdot 3H_2O$, kobalto tamsiai violetinio $Co_3(PO_4)_2$), kobalto mėlynojo tamsus, kobalto melsvai žalio ir smaltos $CoO\cdot nSiO_2$ nustatymui. IR spektroskopiniai tyrimai parodė, kad šis metodas yra efektyvus, kokybiškai nustatant neoksidinius kobalto pigmentus aureoliną $[K_3(Co(NO_2)_6]\cdot 3H_2O$, kobalto šviesiai violetinį $CoNH_4PO_4\cdot H_2O$, kobalto tamsiai violetinį $Co_3(PO_4)_2$ jų švino glazūrose. Paprastu nusodinimo metodu susintetintas

kobalto pigmentas violetinis šviesusis $CoNH_4PO_4$, pasižymintis analogiškomis fizikinėmis savybėmis, kaip ir analogiškas komercinis Kremer Pigmente pigmentas. Sukurtas naujas, patogus ir pakankamai tikslus IR spektroskopinis $SiO_2$ kiekio CoO ir $SiO_2$ mišiniuose (ribose tarp 9,1-50 mol%) ir kobalto pigmente smaltoje $CoO{\cdot}nSiO_2$ (ribose tarp 20 iki 50 mol%) nustatymo metodas. Zolių-gelių metodu susintetinti ir visapusiškai ištirti nauji kobalto pigmentai: špinelio struktūros kobalto aliuminatas $CoAl_2O_4$ ir chromatas $CoCr_2O_4$ bei kobalto, aliuminio ir neodimio oksidų mišiniai ($CoAl_{1,75}Nd_{0,25}O_4$, $CoAl_{1,5}Nd_{0,5}O_4$, $CoAlNdO_4$), pasižymintys spalvinėmis keraminių pigmentų savybėmis. Pirmą kartą zolių-gelių metodu susintetinti ir visapusiškai ištirti nauji kobalto pigmentai: vienfazis perovskito struktūros neodimio kobaltatas $NdCoO_3$, mišrūs perovskitiniai neodimio kobaltatai–aliuminatai ($NdCo_{0,75}Al_{0,25}O_3$, $NdCo_{0,5}Al_{0,5}O_3$, $NdCo_{0,25}Al_{0,75}O_3$), mišrūs neodimio-itrio kobaltatas $(Nd_{0,5}Y_{0,5})CoO_3$ bei neodimio-itrio kobaltatai–aliuminatai $(Nd_{0,5}Y_{0,5})Co_{0,75}Al_{0,25}O_3$, $(Nd_{0,5}Y_{0,5})Co_{0,5}Al_{0,5}O_3$, $(Nd_{0,5}Y_{0,5})Co_{0,25}Al_{0,75}O_3$, pasižymintys išraiškinga mėlyna spalva, būdinga kobalto mėlynajam pigmentui. Parodyta, kad panašiomis sąlygomis erbio kobaltato $ErCoO_3$ sintezė zolių-gelių metodu yra problematiška. Vietoje erbio kobaltato susiformavo tik $Er_2O_3$ ir $Co_3O_4$ mišinys. SEM metodas nėra efektyvus charakterizuojant kobalto pigmentus jų glazūrose, kadangi kobalto glazūrų morfologinius ypatumus apsprendžia ne kobalto pigmentai, bet pagrindinės glazūrų sudedamosios dalys: švino ir silicio oksidai, o visų kobalto glazūrų paviršiaus morfologija yra labai panaši, nepriklausomai nuo naudojamo kobalto pigmento prigimties.