Glass treated on its surface with silver compounds and an aluminosilicate, such as ochre or clay, at higher temperatures (between 550 and 650 °C) accepts a wide variety of a yellow colour. It is the aim of this study to investigate the parameters of the manufacturing process affecting the final colour of silver stained glass and to correlate them with the final colour and colour intensity. Therefore, defined mixtures of ochre and a silver compound (AgCl, AgNO₃, Ag₂SO₄, Ag₃PO₄, Ag₂O) were prepared and applied on soda-lime glass. The firing process was modified within the range from 563 to 630 °C and glass samples were analysed after treatment with energy dispersive X-ray fluorescence analysis (EDXRF), scanning electron microscopy (SEM/EDX), transmission electron microscopy (TEM), as well as ion beam analysis (IBA) with an external beam. Within the scope of IBA simultaneous measurements using particle-induced X-ray emission (PIXE), particle-induced gamma-ray emission (PIGE), and Rutherford backscattering spectrometry (RBS) were carried out in order to obtain the thickness of the Ag-rich surface layer and the depth distribution of Ag. By means of TEM the microstructure of the silver particles was visualised. XRF results show that the lowest amount of Ag could be detected on glass samples treated with silver stain mixtures containing AgCl and Ag₂O. A low kiln temperature (e.g. 563 °C) results in a higher silver concentration at the surface and lower penetration depths. Furthermore, the results obtained with SEM/EDX at cross-sections of the glass samples could be confirmed by PIXE, PIGE, RBS, and TEM.

1. Introduction

The first application of silver stain in Northwestern Europe can be found in stained glass windows of the first half of the 14th century, located in churches. Silver staining has been a convenient method for glass artists to achieve a permanent yellow colour by applying silver compounds mixed with a carrier medium such as ochre or clay (aluminosilicate) on to the glass surface and treating the panels at temperatures just below the softening range of the glass. Two reduction mechanisms are possible: a redox reaction between Ag⁺ and Fe²⁺, As³⁺, Sb³⁺ or a redox reaction of Ag⁺ with non-bridging oxygens in the silicate network. (4) Metallic silver aggregates, forming spherical, metallic crystals with a diameter between 1–100 nm. Depending on the size, shape, and particle size distribution, these nanoparticles affect the colour of silver stain. Although a considerable amount of literature deals with the production and properties of silver stained glass, the historical production method found in the recipes and its parameters affecting the colour have not been treated in detail. For a glass conservator it is of particular importance to understand this production process in order to produce a desired colour for glass pieces which have to be replaced during the conservation of the glass windows. Therefore, silver stained glass samples were made systematically by changing the composition of the silver stain and firing temperature between 563 and 630 °C.

Measurements carried out with energy dispersive XRF were used to characterise the elemental composition of the silver stained glass surface compared to the bulk. X-ray intensities of the Ag Kβ-lines were compared for samples produced at the temperatures of 563, 580, 597, 613, and 630 °C. By means of line scan analysis in SEM, carried out on cross-sections of small
splinters cut from the samples, the penetration depth of silver for different silver salts with increase in the firing temperature was determined. Quantitative evaluations were carried out on the bulk glass of the silver stained samples by SEM/EDX and PIXE/PIGE. These results were used as input for the simulation of the measured RBS spectra carried out with RUMP. In order to prove the results obtained by the line scan analysis in the SEM and to quantify the silver amount considering the silver distribution in the glass surface. Furthermore, TEM investigations delivered detailed information of the microstructure of the silver yellow parts in the treated glasses.

2. Experimental

2.1 Preparation of the glass samples

In order to study the influence of the silver salt and the firing temperature on the colour of the glass and the chemical structure of the glass surface, small plates of silicate glass were treated with AgNO₃, AgCl, Ag₂SO₄, Ag₃PO₄ or Ag₂O mixed with ochre. However, to reduce the number of experiments it was necessary to limit the numbers of variables. Therefore, the samples treated with silver stain mixtures with the weight ratio of silver compound/ochre of 1:2 and 1:3 were investigated. The samples with the weight ratio 1:2 were fired at kiln temperatures of 563, 580, 597, 613, and 630 °C, whereas for the samples with the ratio of 1:3 the firing temperature of 580 °C was chosen.

The soda-lime glass platelets (length 5 cm, width 2 cm, thickness 0.2 cm) were cut from the same glass panel, made by St.-Just, France, No. STD 241 P3 20. Since several silver compounds were mentioned in the historical literature about the production of glass paints, it was supposed that the type of silver compound played an important role in the final colour of silver stained glass. The silver compounds AgNO₃, AgCl, Ag₂SO₄, Ag₃PO₄, and Ag₂O, commercial products from Acros Organics Filter Service n.v./s.a., Handelstraße 16, 4700 Eupen, Belgium, were used. The silver stain mixtures were self-made mixtures of each silver compound and yellow ochre (Al₂O₃–SiO₂–Fe₂O₃) from Linova Verfprodukte, Gelderhorst 12, 7207 BH Zutphen, The Netherlands. For applying the silver stain mixture on the glass samples, an addition of a small amount of water is necessary in order to make the powdery stain mixture pasty. The air-dried samples were fired at the kiln temperatures as mentioned above for 10 min. During preheating, the temperature was increased by 8 °C per minute until the firing temperature is reached. After firing time a slow cooling process is started which takes about 10–12 h. To remove the paste after the firing process the samples were rinsed with water and finally flushed with acetone.

2.2 XRF measurements

Energy dispersive X-ray fluorescence analysis (EDXRF) was carried out using TRACOR XRAY SPECTRACE 5000 equipment from NORAN Instruments, with a Rh-tube and Si(Li) detector (resolution: 150 eV at 5.89 keV). EDXRF was used to characterise both the silver stained glass surface (“front side”) as well as the colourless back side of the samples with the weight ratio 1:2. The spectra were collected at a tube voltage of 50 kV in order to evaluate the Ag Kα-line as the Ag Kβ-line coincides with the Rh-lines (Compton scattering lines) and the Ag Lα-line collected at a tube voltage of 8 kV shows a low intensity. To demonstrate these X-ray line coincidences, the XRF-spectrum of the silver stained glass sample produced by using silver sulfate in the silver stain mixture is shown in Fig. 1. A Pd thin (50 µm) filter was placed between the Rh-tube and the specimen. The time of acquisition was set to 100 s and the tube current to 0.04 mA.

2.3 SEM/EDX measurements

For analysis in the scanning electron microscope the samples fired at the lowest temperature of 563 °C, at the middle temperature of 597 °C, and at the highest firing temperature of 630 °C were chosen from the sample set with ratio 1:2 in order to obtain the influence of the firing process on the silver penetration depth into the glass surface. These samples were cut by a low speed diamond saw perpendicular to the silver stained glass surface. The glass splinters were embedded in resin, polished with SiC paper (4000 mesh) and carbon-coated to prevent charging of the glass surface during the analysis.

The cross-sections were analysed by means of a JSM 6300 JOEL electron microprobe system equipped with an energy dispersive Si(Li) X-ray detector from Princeton Gamma Tech (PGT) (MITAC/Antwerp). In order to perform the quantitative evaluation of the bulk glass, X-ray spectra were collected for 200–300 s using a beam current of 1 nA, an accelerating voltage of 20 kV and a magnification below 5000. A quantification algorithm based on thin film sensitivity coefficients was used to calculate the composition of the bulk glass on the basis of the net intensities of the characteristic X-ray peaks observed in the spectra.

Line scans were performed using a JSM 6400 of JEOL. X-rays were detected with an Oxford Instruments Link eXL energy dispersive system. The investigations were carried out at an accelerating voltage of 20 kV, a beam current of 3 nA, a
working distance of 39 mm and a live time of 100 s for each run. 20 runs were added up for one line scan.

In both cases, while collecting the X-ray spectra as well as the line scans, the measurement conditions mentioned prevent the migration of Na ions due to the electron bombardment during the analysis.

2.4 TEM investigations

The CTEM investigations were carried out on the samples prepared with the ratio 1:3, using a Philips CM20 microscope, working at 200 kV, equipped with an Oxford energy dispersive X-ray (EDX) detector and a Link Analytical System. The HRTEM images are obtained with a JEOL 4000EX microscope, operated at 400 kV. CTEM requires a sample thickness of less than 150 nm, while for HRTEM the thickness should not exceed 50 nm because these techniques work in transmission. For reducing the sample size the methods “crushing” and “ion milling” were used. “Crushing” implies that the sample is ground in order to obtain particles that are small enough to analyse them in transmission. This method was applied in the study of individual silver particles. In order to obtain information about the silver particles as a function of depth, the “ion milling” method was used. The reduction of the sample thickness by this method is based on argon ion bombardment with a beam of 5 kV and an incidence angle of 8°.

2.5 IBA measurements

Silver stained samples with the weight ratio 1:2 fired at 597 °C were selected for ion beam analysis (IBA) in order to obtain detailed information about the silver concentration in the silver stained surface. At the 5 MV tandem accelerator of the Research Centre Rossendorf, Germany, PIXE, PIGE and RBS can be carried out simultaneously. The measurements were performed with an external proton beam of 3.85 MeV and 0.5 nA beam current within a beam spot of 1.8 mm². Typical acquisition times amounted to 600 s. The external beam set-up, used for analyzing objects of art, consists of two Si(Li) detectors for the detection of X-rays, a silicon surface barrier detector for detecting backscattered protons, and a large volume HPGe detector for analyzing γ-radiation. All the detectors are positioned at backward angles. A detailed description of the Rossendorf external IBA facility is given by Neelmeijer et al. A continuous gas flow (3 l min⁻¹) of helium was used between the glass sample and both the beam exit window and the detectors PIXE1 and RBS. This arrangement reduces X-ray absorption, it avoids Ar K-radiation in the PIXE spectra and the detectors PIXE1 and RBS. This method was applied in the study of individual silver particles. In order to obtain information about the silver particles as a function of depth, the “ion milling” method was used. The reduction of the sample thickness by this method is based on argon ion bombardment with a beam of 5 kV and an incidence angle of 8°.

The measurements were carried out on the specimens without any additional sample preparation. PIXE, PIGE and RBS spectra were taken from the silver stained glass surface and, in addition from the back side, representative for the bulk glass. Using the combination of PIXE and RBS for simultaneous measurements, both the elemental composition and the thickness of the silver containing glass surface can be determined.

Evaluation of the PIXE spectra was carried out by using GUPIX. For the quantitative evaluation of the bulk glass the “matrix” option of GUPIX was applied. Elements, which cannot be detected by PIXE in the described set-up, such as Mg and Al, were evaluated by comparing the PIGE spectra with glass standards measured at the same experimental conditions. PIXE spectra obtained from the silver stained glass surface were evaluated (i) by using the element concentrations calculated by the GUPIX matrix version for the bulk glass and (ii) subsequent GUPIX (“trace” option) calculation of Ag concentrations C_Ag from both the Ag-K and the Ag-L radiation under gradual variation of the target thickness.

The measurements were carried out on the specimens prepared with the ratio 1:3, using a Philips CM20 microscope, working at 200 kV, equipped with an Oxford energy dispersive X-ray (EDX) detector and a Link Analytical System. The HRTEM images are obtained with a JEOL 4000EX microscope, operated at 400 kV. CTEM requires a sample thickness of less than 150 nm, while for HRTEM the thickness should not exceed 50 nm because these techniques work in transmission. For reducing the sample size the methods “crushing” and “ion milling” were used. “Crushing” implies that the sample is ground in order to obtain particles that are small enough to analyse them in transmission. This method was applied in the study of individual silver particles. In order to obtain information about the silver particles as a function of depth, the “ion milling” method was used. The reduction of the sample thickness by this method is based on argon ion bombardment with a beam of 5 kV and an incidence angle of 8°.

2.5 IBA measurements

Silver stained samples with the weight ratio 1:2 fired at 597 °C were selected for ion beam analysis (IBA) in order to obtain detailed information about the silver concentration in the silver stained surface. At the 5 MV tandem accelerator of the Research Centre Rossendorf, Germany, PIXE, PIGE and RBS can be carried out simultaneously. The measurements were performed with an external proton beam of 3.85 MeV and 0.5 nA beam current within a beam spot of 1.8 mm². Typical acquisition times amounted to 600 s. The external beam set-up, used for analyzing objects of art, consists of two Si(Li) detectors for the detection of X-rays, a silicon surface barrier detector for detecting backscattered protons, and a large volume HPGe detector for analyzing γ-radiation. All the detectors are positioned at backward angles. A detailed description of the Rossendorf external IBA facility is given by Neelmeijer et al. A continuous gas flow (3 l min⁻¹) of helium was used between the glass sample and both the beam exit window and the detectors PIXE1 and RBS. This arrangement reduces X-ray absorption, it avoids Ar K-radiation in the PIXE spectra and the detectors PIXE1 and RBS. This method was applied in the study of individual silver particles. In order to obtain information about the silver particles as a function of depth, the “ion milling” method was used. The reduction of the sample thickness by this method is based on argon ion bombardment with a beam of 5 kV and an incidence angle of 8°.

The measurements were carried out on the specimens without any additional sample preparation. PIXE, PIGE and RBS spectra were taken from the silver stained glass surface and, in addition from the back side, representative for the bulk glass. Using the combination of PIXE and RBS for simultaneous measurements, both the elemental composition and the thickness of the silver containing glass surface can be determined.

Evaluation of the PIXE spectra was carried out by using GUPIX. For the quantitative evaluation of the bulk glass the “matrix” option of GUPIX was applied. Elements, which cannot be detected by PIXE in the described set-up, such as Mg and Al, were evaluated by comparing the PIGE spectra with glass standards measured at the same experimental conditions. PIXE spectra obtained from the silver stained glass surface were evaluated (i) by using the element concentrations calculated by the GUPIX matrix version for the bulk glass and (ii) subsequent GUPIX (“trace” option) calculation of Ag concentrations C_Ag from both the Ag-K and the Ag-L radiation under gradual variation of the target thickness. From the target thickness where C_Ag(Ag-K) = C_Ag(Ag-L) is reached it can be deduced both the real Ag content and the real thickness of the thin silver doped glass surface region of the glass matrix. The GUPIX results were used as starting values for subsequent RUMP simulations of the measured RBS spectra.

A detailed discussion about accuracy, precision and detection limits of the RBS and PIGE techniques can be found by Tesmer et al., that of SEM/EDX by Kuisma-Kursula, and those of PIXE by Kuisma-Kursula and Johansson et al.

3. Results and discussion

3.1 Visual observations

As already mentioned in the literature, the final colour of silver stained glass surface ranges from pale yellow over bright yellow to dark brown when the amount of silver compound in the mixture is increased. Also, by increasing the firing temperature, the colour intensity increases to more brownish but also the type of silver compound used affects the colour. Furthermore, for all silver compounds, the visual observations have shown inhomogeneities in the coloured surface. The Ag₂O, AgCl, Ag₃PO₄, and Ag₄SO₄ resulted in a coloured layer that was speckled, whereas AgNO₃ formed a homogenous coloured layer because its solubility in water results in a better distribution of the silver salt in the mixture. Since every silver salt grain acts as a point source, the grains should be as small as possible and close to each other. In Fig. 2 a backscattered electron image is shown of a speckled surface that was made by firing an Ag₂SO₄ mixture of 1:2 at 630 °C.

On the basis of the final colour the silver compounds can be divided into three groups: (1) silver compounds resulting in an intense colour at low firing temperatures such as AgNO₃ and Ag₂SO₄; (2) compounds resulting in a paler colour at low firing temperatures such as AgCl and Ag₃PO₄; and (3) compounds that hardly result in any colour such as Ag₂O.

Fig. 2 Speckled appearance of silver stained glass surface treated with Ag₂SO₄, fired at 630 °C. The ratio of silver compound/ochre was equal to 1:2.

3.2 XRF measurements

The difference in colour intensity obtained by visual observations might be explained by a difference in silver concentration just below the surface. Therefore, X-ray spectra were collected from the silver stained glass surface by means of EDXRF.

Fig. 3 shows the Ag Kβ intensities obtained from the silver stained surfaces treated with Ag₂SO₄, Ag₃PO₄, AgNO₃, AgCl and Ag₂O with a weight ratio of the silver compound/ochre of 1:2.
1:2 and fired at different temperatures. For Ag$_2$SO$_4$, Ag$_3$PO$_4$, AgNO$_3$, and AgCl the intensity of the Ag K$_\beta$ line increases by increasing the firing temperature. The oscillations of the intensities of the Ag K$_\beta$ lines shown in Fig. 3 are caused due to the inhomogeneities in the silver stained surfaces of the samples. As can clearly be seen, the lowest Ag K$_\beta$ intensity has been measured at the specimen treated with Ag$_2$O and AgCl. Due to the weakly coloured surface and a very inhomogeneous silver distribution in the glass obtained from visual observations, the EDXRF measurements performed at the specimen treated with Ag$_2$O are afflicted with high measuring errors. Furthermore, Fig. 3 shows that the type of the silver compound has its effect on the amount of silver in the glass. On the basis of these measurements, the colouring behaviour of the silver compounds can be ordered, from strong to weak, Ag$_2$SO$_4$, Ag$_3$PO$_4$, AgNO$_3$, AgCl, and Ag$_2$O.

### 3.3 SEM measurements

The concentration gradient of silver and alkali ions between the glass substrate and the silver stain mixture at the glass surface is the driving force of the diffusion process. According to the laws of Fick a concentration profile of silver has to be present below the glass surface. Therefore, several measurements were carried out on cross-sections by means of the line scan analysis in SEM. Fig. 4 and 5 summarise the line scans over the cross-sections of silver stain samples produced with Ag$_2$SO$_4$ and AgNO$_3$ at 597 °C for a silver salt/ochre weight ratio of 1:2. As can be seen in the BE image of Fig. 4 Ag$_2$SO$_4$ leads to Ag containing regions with a varying Ag penetration depth as well as inhomogeneities of silver in the glass surface. In between the high Ag containing glass domains, regions which do not contain any silver can be found. The minimum layer thickness of the Ag containing regions is 20.5 μm, while the maximum is 43 μm. Such variation of the Ag depth distribution was only found for glass samples treated with Ag$_2$SO$_4$ and Ag$_3$PO$_4$.

As shown in the BE image of Fig. 5, glass with a mainly homogenous Ag distribution was formed on the surface of samples treated with AgNO$_3$. In this case, the minimum layer thickness is 15.6 μm and the maximum 40.9 μm. The BE-image in the upper part of the Fig. 5 shows that by using AgNO$_3$ in the silver stain mixture a more homogenous silver containing glass surface layer was obtained than by using Ag$_2$SO$_4$ (Fig. 4). This can be explained by the higher solubility of AgNO$_3$ in water than of Ag$_2$SO$_4$, which results in a better distribution of the salt (Ag ions) in the mixture and consequently in a more homogeneous distribution of the AgNO$_3$ on the glass surface. However, according to the line scans no clear conclusions concerning the Na” exchange versus Ag” can be drawn for most samples analysed. As shown in Fig. 4, a decrease of the intensity of the Na K$_\alpha$-line was only obtained for the samples treated with Ag$_2$SO$_4$, because of the large amount of silver which is penetrating into the glass surface. For all other silver compounds the amount of silver going into the glass seems to be insufficient to imply any changes in the intensity of the Na K$_\alpha$-line under described measurement conditions.

In addition, the distribution of silver in the glass surface depending on the firing temperatures is shown in Fig. 6.
Therefore, an example of the cross-sectioned samples produced with Ag2SO4 in the silver stain mixture, and fired at 563, 597, and 630 °C is presented. The label of the y-axis is given by the full scale (FS), which means that the y-axis ranges from 0 to 127 cps (Figs. 6(a) and 6(b)) and from 0 to 63 cps (Fig. 6(c)). As can be seen (Ag Lx), by increasing the firing temperature silver penetrates deeper into the glass surface, whereas the silver X-ray intensities of the surface layer decreases.

Fig. 7 summarises the penetration depths of Ag in the glass surface depending on the firing temperature and the silver compounds. The Ag penetration depths presented were measured in the surface regions with the highest Ag content (see for example Fig. 4). The highest penetration depths of Ag were achieved with Ag2SO4 in the silver stain mixture. Furthermore, an increase of the penetration depth of Ag with the temperature could clearly be determined for AgNO3 and Ag2O. For the silver salts AgCl and Ag3PO4 the highest penetration depths were found at 597 °C.

The line scan shown in Fig. 8 was collected under such circumstances (accelerating voltage of 15 kV, measuring time of 5 s per point) that the change in composition caused by the electron beam is minimal. By normalizing the intensities, the change in X-ray absorption as a function of depth could be compensated. As a result of this, the Mg-K intensity in Fig. 8 that was collected at a Ag2SO4 treated sample (ratio 1 : 2, 630 °C) is nearly constant. Therefore, the decrease in sodium intensity close to the surface can only be explained by the replacement of this element by silver. The line scan demonstrates that the chemical composition of the bulk glass just below the surface underwent an alternation: an enrichment of silver and a depletion of sodium has been detected.

3.4 TEM measurements

Although SEM/EDX is a versatile technique, it is not able to study the silver nanoparticles in silver stained glass due to its limited spatial resolution. Therefore, TEM was applied in the study of the particle size, shape and atomic structure of the silver particles.

For this investigation, two glass samples coloured by Ag2O and by AgNO3, with a silver compound/ochre ratio of 1:3 and fired at the temperature of 580 °C, were selected. These two samples have the largest visual difference in colour, the AgNO3 glass being very intensely coloured, while the Ag2O glass is practically colourless. Using the ion milled cross-sectioned sample, the depth distribution of the particles is investigated. X-ray spectra were collected to identify the silver particles embedded in the glass matrix. An example of such a spectrum is shown in Fig. 9a.

Fig. 6 Line scan analysis carried out on the cross-sections of the silver stain samples produced by Ag2SO4 and ochre at 563 °C (a), 597 °C (b), 630 °C (c) with a silver salt/ochre weight ratio of 1:2. The intensity of the Ag Lx-line corresponds to the silver containing glass surface.

Fig. 8 Depth distribution of the X-ray intensities for Na Kα, Mg Kα and Ag Lx, measured at the cross-section of the silver stained sample treated with Ag2SO4, ratio 1:2, and fired at 630 °C.

Fig. 7 Comparison of the penetration depths of silver into the glass surface for different temperatures and different silver salts. The penetration depths were obtained by line-scan analysis using SEM/EDX.
very small particles (i.e. <3 nm) is expressed in the number of particles per 20 nm × 20 nm, so that their quantities can be displayed in the same graph. A true three-dimensional density is very difficult to establish, since in TEM the influence of the thickness of the sample is hard to estimate. Some indicational values of this “projected density” are plotted in Fig. 10.

The particles have been subdivided according to their sizes into four classes: (1) the large particles (>10 nm), (2) medium particles (between 6 and 9 nm), (3) small particles (between 4 and 6 nm) and (4) the very small particles (<3 nm). For both samples, the projected density of these four classes as a function of depth is shown in Fig. 10. In case of the Ag2O glass, it was difficult to find any particle from a distance of 30 μm onwards, while in the AgNO3 glass, even at a distance of 150 μm, very small particles can be found in rather large numbers (i.e. 5 particles per 20 nm × 20 nm). Thus, the gradient in the AgNO3 glass expands deeper into the material and shows smooth particle density curves. Due to the smaller number of particles present in the Ag2O glass, the gradient is less defined and the curves are more whimsical. The largest particles in the Ag2O glass belong to the class “>10 nm”, while in the AgNO3 sample, the largest particles range mostly from 6 nm to 9 nm. In the Ag2O glass, the class of particles between 4 and 6 nm is practically non-existent; the particles are either larger than 6 nm, or smaller than 3 nm.

A remarkable feature that appears in both materials is the relation between the bigger (i.e. >6 nm) particles and the small particles (i.e. <6 nm). The concentration of large particles has a local maximum close to the surface (3 μm for AgNO3 and 1 μm for Ag2O) and this corresponds to a local minimum in the curve of the projected density of the small particles. The largest density of small particles (i.e. <6 nm) for AgNO3 glass ranges from 6 μm to about 14 μm from the glass surface. This may indicate some form of local, depth dependent “Ostwald ripening”, which causes the large particles to grow at the expense of the smaller ones. The penetration depth as measured by TEM is larger than the depth measured by SEM which can be explained with the fact that SEM/EDX cannot measure concentrations lower than 0.1% m/m.

Apart from the depth distribution of the silver particles, the morphology of individual silver particles was investigated using HRTEM. In this case, a glass fragment was coloured with a commercially available silver stain powder, based on Ag2SO4. This sample was chosen since the particles are less densely packed than the particles in the AgNO3 glass and the very small particles in the Ag2O glass, yet displays all ranges of particle sizes observed before. Since no depth distribution dependent information is desired, crushed samples were used. As seen before (Fig. 9), most particles are quasi-spherical and monocrystalline (Fig. 11a), though sometimes twinned particles are found (see Fig. 11b). Only a few particles have facets (see Fig. 11c) and these particles always belong to the very small class of particles of <3 nm. In larger particles, no facets were found at all.

3.5 IBA measurements

As shown in Table 1 the compositions (% m/m) of the bulk glass deduced from both PIGE and PIXE, as well as SEM/EDX, are in good agreement. Differences regarding the concentration values of Na2O calculated from SEM/EDX and PIGE measurements are mainly caused by the evaluation of the PIGE spectra due to the low intensity of Na on the high background in the PIGE spectra. The high value for Al (% m/m) obtained by SEM/EDX in comparison to the value calculated from PIGE, is due to the evaluation procedure of the SEM data carried out with the AXIL software. The Al Kα peak in the X-ray spectra collected using SEM lies in the low energy range and is therefore not detectable.
Table 1 Comparison of the mean values of the element oxides for the bulk glass calculated from PIGE and PIXE (mean values were calculated from 5 measurements in the bulk) and SEM/EDX (mean values were calculated from 3 measurement points in the bulk).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>PIGE, PIXE</th>
<th>SEM/EDX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na2O</td>
<td>19.0 ± 0.37</td>
<td>16.12 ± 0.16</td>
</tr>
<tr>
<td>MgO</td>
<td>1.73 ± 0.13</td>
<td>1.79 ± 0.10</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.53 ± 0.07</td>
<td>1.29 ± 0.10</td>
</tr>
<tr>
<td>SiO2</td>
<td>67.7 ± 1.34</td>
<td>71.6 ± 0.15</td>
</tr>
<tr>
<td>K2O</td>
<td>0.10 ± 0.01</td>
<td>0.15 ± 0.00</td>
</tr>
<tr>
<td>CaO</td>
<td>8.15 ± 0.14</td>
<td>8.77 ± 0.29</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>0.21 ± 0.01</td>
<td>0.24 ± 0.15</td>
</tr>
<tr>
<td>Sb2O5</td>
<td>0.61 ± 0.07</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

Table 2 Comparison of the thickness values and the concentrations of Ag in the Ag containing glass regions calculated by GUPIX. Silver stained samples were produced by using different silver salts in the silver stain mixture with silver salt/ochre weight ratio 1:2, fired at 597°C. The data in μm scale are calculated by assuming ρ(glass) = ρ(SiO2) = 2.19 g cm⁻³.

<table>
<thead>
<tr>
<th>Glass no.</th>
<th>Concentration of the Ag in the glass surface (% m/m)</th>
<th>Thickness of the Ag containing glass surface μm</th>
<th>Information depth substrate/μm²</th>
<th>Ag-content (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 70 (AgCl)</td>
<td>2.38</td>
<td>5600</td>
<td>25.57</td>
<td>29520</td>
</tr>
<tr>
<td>No. 71 (Ag2O3)</td>
<td>2.99</td>
<td>7400</td>
<td>33.79</td>
<td>29490</td>
</tr>
<tr>
<td>No. 72 (Ag2O4)</td>
<td>2.84</td>
<td>5900</td>
<td>26.94</td>
<td>29520</td>
</tr>
<tr>
<td>No. 73 (Ag3O)</td>
<td>0.93</td>
<td>4300</td>
<td>19.63</td>
<td>29580</td>
</tr>
<tr>
<td>No. 75 (Ag2SO4)</td>
<td>6.17</td>
<td>6300</td>
<td>28.77</td>
<td>29410</td>
</tr>
</tbody>
</table>

Fig. 12 RBS spectrum of Ag containing glass surface of sample no. 70, produced using AgCl and ochre in the silver stain mixture (weight ratio 1:2) and fired at 597°C, as measured (broken line) and simulated by RUMP (full line). The simulation shows the result of the two-layer calculation (see text). The thickness of the Ag doped layer is 25.6 μm containing 0.64 at% Ag.
when fired at a low firing temperature; and (3) Ag$_2$O hardly resulted in any colour. Furthermore, AgNO$_3$ was the only silver compound that resulted in silver stained samples with a homogeneous colour (visual observations). For the other silver compounds, the particle size of the powder was not small enough and a speckled pattern was obtained. The difference in colour could be correlated to the total concentration of the silver penetrated into the glass (PIXE) as well as to the size of the silver particles (CTEM). Higher silver concentrations correspond with more intense and brownish colours. The combination of SEM/EDX, RBS and TEM has shown that a gradient in the silver concentration is present in the glass. Close to the surface the concentration of silver is high (RBS) and the number and size of silver particles is large (> 10 nm, CTEM). At deeper regions the silver concentration drops but also the size and the number of the silver particles becomes smaller. The penetration depths measured by TEM are larger than that of SEM/EDX because SEM/EDX is limited by a detection limit of 0.1% m/m. The TEM measurements suggest that the large particles (> 10 nm) close to the surface grew at the expense of the smaller ones. More detailed investigations using HRTEM show that most particles created in this way are monocrystalline and spherical. The penetration depth of silver increases with the firing temperature.

**4. Conclusion**

The experiments discussed in this paper have clearly demonstrated that parameters such as the type of silver compound that has been used and the firing temperature play a crucial role on the final colour of silver stained glass. On the basis of the visual observations of the final colour, the silver compounds could be divided in three groups: (1) AgNO$_3$ and Ag$_2$SO$_4$ resulted in an intense colour when fired at a low firing temperature; (2) AgCl and Ag$_3$PO$_4$ resulted in a paler colour when fired at a low firing temperature; and (3) Ag$_2$O hardly resulted in any colour. Furthermore, AgNO$_3$ was the only silver compound that resulted in silver stained samples with a homogeneous colour (visual observations). For the other silver compounds, the particle size of the powder was not small enough and a speckled pattern was obtained. The difference in colour could be correlated to the total concentration of the silver penetrated into the glass (PIXE) as well as to the size of the silver particles (CTEM). Higher silver concentrations correspond with more intense and brownish colours. The combination of SEM/EDX, RBS and TEM has shown that a gradient in the silver concentration is present in the glass. Close to the surface the concentration of silver is high (RBS) and the number and size of silver particles is large (> 10 nm, CTEM). At deeper regions the silver concentration drops but also the size and the number of the silver particles becomes smaller. The penetration depths measured by TEM are larger than that of SEM/EDX because SEM/EDX is limited by a detection limit of 0.1% m/m. The TEM measurements suggest that the large particles (> 10 nm) close to the surface grew at the expense of the smaller ones. More detailed investigations using HRTEM show that most particles created in this way are monocrystalline and spherical. The penetration depth of silver increases with the firing temperature.

**Acknowledgement**

The authors gratefully acknowledge Mrs. Ing. E. Eitenberger for her supports during SEM measurements. Measurements using Ion Beam Analysis performed at the Research Centre Rossendorf were supported by the European Community FMGE-CT98-0146 (Large Scale Facility AIM Rossendorf).

**References**