X-RAY SPECTROMETRY
X-Ray Spectrom. 2003; **32**: 373–380
DOI: 10.1002/xrs.654

Determination of the provenance of medieval silver coins: potential and limitations of x-ray analysis using photons, electrons or protons

R. Linke,[1]* M. Schreiner,[1] G. Demortier[2] and M. Alram[3]

[1] Institute of Humanities, Sciences and Technologies in Art, Academy of Fine Arts Vienna, Schillerplatz 3, A-1010 Vienna, Austria
[2] LARN, Facultés Universitaires Notre-Dame de la Paix, 61 rue de Bruxelles, B-5000 Namur, Belgium
[3] Coin Cabinet, Kunsthistorisches Museum Vienna, Burgring 5, A-1010 Vienna, Austria

Received 10 October 2002; Accepted 25 March 2003

One hundred and fifty seven 'Tiroler Kreuzer', a medieval currency from the county of Tyrol/Austria, were analysed in order to determine their place of mintage. The silver coins were produced during the 15th century in the mints of Merano (South Tyrol) and Hall (North Tyrol) but they have no marks or punches which would allow a clear distinction. Energy-dispersive x-ray fluorescence analysis (EDXRF) was applied without sampling in order to determine the silver contents and also minor (Cu, Pb, Bi) and trace elements (Fe, Au, Hg, Ni). Owing to corrosion processes, which changed the chemical composition of the surfaces of the coins, investigations of cross-sections were necessary using energy-dispersive x-ray microanalysis in a scanning electron microscope (SEM/EDX) to determine the stage of corrosion and the Ag concentration of the core of the coins. The results showed differences of up to 50% between the composition of the core and the surface. Finally, proton-induced x-ray emission (PIXE) at an external proton beam was applied, in order to detect also Ni, an element which could not be measured by either EDXRF or SEM/EDX in the ppm range. The data show a clear difference in the Ni content between the coins from Merano (∼0.1% Ni) and Hall (∼0.01% Ni).

INTRODUCTION

In cooperation with the Coincabinet of the Kunsthistorisches Museum Vienna, scientific investigations were to be carried out on the 'Tiroler Kreuzer' (Fig. 1) of Archduke Sigismund of Tyrol (1439–90, †1496) minted in Hall and Merano between 1446–50 and 1487. The coins are part of a hoard found in Lower Austria in 1992. The hoard contains 2797 silver and 14 gold coins, which were stored in a jar buried in soil. Owing to the huge number of variants, this hoard allows the unique possibility for numismatists to survey the complete mintage of Archduke Sigismund and to set up a chronology of his coinage.

According to the chronology of emission, the mintage of Archduke Sigismund can be separated into 10 main groups (I–X), where the coins of the groups I–VII were minted in the town of Merano (South Tyrol). Within group VIII, which consists of three variants (subgroups), the mint was transferred from Merano to Hall (North Tyrol) in December 1477.[1] It is assumed by numismatists that subgroup VIII/1 was still produced in Merano and subgroup VIII/3 already in Hall. However, there exists no evidence for this postulation and it is completely uncertain whether the coins of subgroup VIII/2 were still minted in Merano or in Hall. The silver content of the coins is of major importance for historians in order to draw conclusions from the economic situation in the second half of the 15th century in Tyrol. Wieser[2] and Rizzolli[3] have reported an initial silver concentration of 75% in the coins, which was reduced to 50% not later than in 1473. However, the precise date of this depreciation is unknown.

Scientific investigations should be carried out in order to determine the silver contents of the coins and to deduce the provenance of the coins of the subgroups VIII/1 to VIII/3. Previous studies[4] have shown that the chemical composition of the silver alloys can be regarded as being characteristic of the various mintages of the medieval period. These characteristics can originate from the different ores and from the manufacturing process used for the silver production. In the 15th century, the lead ore deposits near Schwaz in North Tyrol produced silver for both Merano and Hall mints. Further, it has to be considered that silver was also imported by merchants and that usually old coins were recycled, which makes an assignment of the coins due to their material composition more difficult. For a statistical evaluation of the data a representative number of coins are required as untypical values influence the interpretation of the analytical results. However, this requirement could not be complied with in all cases owing to the rarity of most groups of coins.

ANALYTICAL STRATEGY

Analytical studies on objects of art and archaeology represent, in general, a challenge for modern analytical techniques. As the objects are usually unique and of high

---

*Correspondence to: R. Linke, Institute of Humanities, Sciences and Technologies in Art, Academy of Fine Arts Vienna, Schillerplatz 3, A-1010 Vienna, Austria. E-mail: r.linke@akbild.ac.at

Figure 1. 'Tiroler Kreuzer' by Archduke Sigismund of Tyrol.

value, investigations must be non-destructive, i.e. no original sample material should be removed and the object itself should not be modified in any way during examination. The most common techniques for this very specific field of analytical chemistry are x-ray fluorescence analysis (XRF),[5,6] energy-dispersive x-ray microanalysis in a scanning electron microscope (SEM/EDX),[7–9] neutron activation analysis (NAA)[10] and particle-induced x-ray emission (PIXE).[11,12] The application of these methods, frequently in combination with other techniques where sampling is required, enables information to be obtained concerning the material composition, manufacturing and hence intended purpose, age or authenticity.

As the 'Tiroler Kreuzer' coins are particularly rare and therefore of high value, it was intended to perform the analyses without sampling. The first step for the chemical characterization of the coins was energy-dispersive x-ray fluorescence analysis (EDXRF) as this technique allows rapid qualitative and quantitative multielement analysis. All coins investigated were in a worn but good condition and no visible signs of corrosion could be observed. After the excavation in 1992, all objects had been cleaned by the conservator of the Kunsthistorisches Museum using a solution of Complexone-III and ethanol. The coins were coated with a layer of microcrystalline wax for conservation reasons and, therefore, all coins had to be cleaned using benzine and ethanol in an ultrasonic bath prior to analysis.

EXPERIMENTAL

We analysed 119 coins by means of EDXRF, which were selected to obtain a statistical distribution between all groups of coins. Analyses were performed using a Spectrace 5000 energy-dispersive instrument (Tracor X-ray) including an Si(Li) detector of 150 eV resolution at 5.89 keV (Mn Kα line). An Rh tube with an acceleration voltage of 50 kV and a primary filter of Pd with 50 μm thickness were used for excitation. Owing to the varying surface structures and inhomogeneities in the surface composition of the coins, analyses were performed on both sides of the objects and mean values were calculated. The area of x-ray irradiation had a circular shape with a diameter of ~10 mm as the coins were rotated on a sample tray at a rate of ~6 rotations per minute in order to compensate for any irregularities which may occur on the coin surface.

For SEM/EDX analysis, a JSM 6400 scanning electron microscope (Jeol) with a Link eXL energy-dispersive x-ray microanalyser was used. Fifty-two coins were selected (see Table 1) based on their state of preservation. A small splinter was cut from each coin by means of a scalpel. Samples were embedded in resin, ground and polished using SiC paper of 4000 mesh perpendicular to their surfaces so that the SEM investigations could be performed on the polished cross-sections. For quantitative analysis, areas of ~214 × 164 μm (magnification 500×) to 107 × 82 μm (magnification 1000×) were scanned. In general, five measurements were performed at each cross-section and mean values were calculated. It was necessary to perform quantitative analyses on areas that were not yet affected from corrosion. Quantification was carried out using silver–copper standards and element profiles (virtual standards), stored in the software package Link Rel.1.35, and applying ZAF-4 correction.

PIXE analyses took place at the Laboratoire d'Analyses par Réactions Nucléaires (LARN) in Namur (Belgium). Measurements were performed in air using an external beam of 2.9 MeV proton energy and a beam diameter less than 1 mm. A 10 μm cobalt absorber (K absorption edge, 7.7 keV) between the coin and the Si(Li) detector was used in order to achieve relative enhancement of the characteristic x-ray intensities of elements lighter than copper (Ni Kα, 7.5 keV) and to suppress the intensities of the Kα and Kβ lines of copper (Cu Kα, 8.0 keV; Cu Kβ, 8.9 keV), i.e. of the most abundant element in the coins apart from silver. Each coin was mounted on a frame in order to keep the geometric conditions constant during all the analyses of the coins and the reference materials. The coins were analysed on the obverse and reverse and mean values were calculated. The experimental set-up has been described previously.[13] For quantitative evaluation, 'Pixboy'[14,15] was applied, i.e. a self-made iterative program, which takes into account several parameters such as x-ray cross-sections, x-ray absorption, secondary fluorescence, sum and escape peaks. The program allows a quantitative determination of the alloy by comparison with signals from their respective neighbouring elements using the appropriate corrections. All the measurements were normalized in order to obtain total concentrations of 100%.

RESULTS AND DISCUSSION

Energy-dispersive x-ray fluorescence analysis

The main elements of the objects, silver and copper, were quantified by using silver–copper standards made by ÖGUSSA (Österreichische Gold- und Silberscheideanstalt). The minor and trace elements iron, gold, mercury, lead and bismuth were determined from their x-ray intensities, which seemed to be sufficient for the present analytical problem.

The silver content of the coins was found to vary in the range 55.5 ± 6.1 to 81.3 ± 1.2 wt%. Detailed results have been published elsewhere.[16] Figure 2 shows the silver contents of the coins, listed in order of their emission. Obviously, no conclusions can be drawn as to the chronology of emission from that figure. As the silver contents of the coins vary

Table 1. 'Tiroler Kreuzer' analysed by EDXRF, SEM/EDX and PIXE[a]

Analysis no.	Group	Mint	EDXRF		SEM/EDX	PIXE					
			Ag (% ±SD)	Ag K/L (%)[b]	Ag (% ±SD)	Ag (%)	Cu (%)	Pb (%)	Ni (%)	Bi (%)	Sb (%)
S4	VIII/2	?	—	—	49.6 ± 4.0	92.2	6.35	0.50	0.042	0.55	0.25
S5	VIII/2	?	—	—	48.4 ± 3.3	94.6	4.20	0.35	0.143	0.45	0.00
S6	IX/1	Hall	—	—	40.2 ± 2.7	91.6	5.60	1.25	0.011	1.05	0.30
S7	IX/1	Hall	—	—	66.2 ± 1.6	87.2	11.15	0.65	0.005	0.55	0.25
S8	X/1	Hall	—	—	87.0 ± 6.9	89.8	8.45	0.70	0.000	0.70	0.20
S9	V	Merano	—	—	71.7 ± 5.4	92.3	5.90	0.60	0.066	0.75	0.15
S10	V	Merano	—	—	71.7 ± 3.5	92.1	6.45	0.80	0.026	0.10	0.40
S11	V	Merano	—	—	74.9 ± 3.2	90.4	7.35	0.45	0.083	0.50	0.00
S12	VIII/1	Merano (?)	—	—	45.3 ± 5.1	93.1	4.95	1.35	0.011	0.30	0.15
S13	VIII/1	Merano (?)	—	—	49.7 ± 2.3	94.6	3.75	0.65	0.178	0.40	0.15
S14	VIII/1	Merano (?)	—	—	70.1 ± 1.8	93.1	4.75	1.30	0.016	0.35	0.35
S15	VIII/1	Merano (?)	—	—	46.4 ± 1.0	90.5	7.55	0.85	0.016	0.30	0.60
S16	VIII/2	?	—	—	39.4 ± 3.6	91.9	6.10	0.95	0.059	0.50	0.40
S17	VIII/3	?	—	—	39.8 ± 2.5	87.4	10.45	0.65	0.012	1.05	0.25
S18	VIII/3	Hall (?)	—	—	37.4 ± 2.4	92.4	5.10	1.15	0.029	0.85	0.30
S19	VIII/3	Hall (?)	—	—	37.6 ± 2.1	90.9	6.30	1.15	0.036	0.85	0.55
S20	IX/1	Hall	—	—	74.6 ± 2.7	—	—	—	—	—	—
S21	IX/1	Hall	—	—	37.6 ± 1.1	89.8	7.75	1.70	0.022	0.25	0.35
S22	IX/2	Hall	—	—	39.7 ± 1.3	91.0	7.60	0.40	0.008	0.65	0.10
S23	IX/5	Hall	—	—	41.4 ± 4.4	94.1	4.40	0.60	0.038	0.65	0.00
S24	IX/5	Hall	—	—	43.2 ± 2.4	92.6	4.75	0.90	0.012	1.20	0.35
S25	X/1	Hall	—	—	49.5 ± 1.0	94.7	3.95	0.50	0.007	0.65	0.00
S26	X/1	Hall	—	—	50.0 ± 0.8	93.5	5.20	0.65	0.005	0.35	0.05
S27	X/1	Hall	—	—	39.0 ± 3.3	94.5	3.65	0.85	0.000	0.65	0.20
S28	X/1	Hall	—	—	73.0 ± 3.3	88.4	8.95	0.95	0.000	1.15	0.35
S29	II/38	Merano	77.3 ± 1.2	94.5	74.8 ± 2.5	89.9	8.60	0.60	0.032	0.40	0.25
S30	IV/3	Merano	78.4 ± 1.4	97.8	76.0 ± 1.6	92.0	6.85	0.30	0.068	0.40	0.25
S31	V	Merano	76.5 ± 4.5	93.7	71.6 ± 4.6	93.5	5.50	0.20	0.154	0.10	0.30
S32	VIII/1	Merano (?)	72.7 ± 3.1	88.2	41.7 ± 3.1	90.9	6.70	1.30	0.006	0.35	0.50
S33	VIII/1	Merano (?)	73.1 ± 1.5	84.3	45.3 ± 4.5	91.9	6.40	1.00	0.004	0.35	0.15
S34	VIII/2	?	79.6 ± 2.1	86.2	40.6 ± 1.6	94.3	4.05	0.55	0.056	0.90	0.00
S35	VIII/2	?	67.8 ± 0.8	80.0	35.3 ± 1.5	83.1	15.30	0.70	0.127	0.45	0.20
S36	VIII/2	?	79.0 ± 0.8	90.4	44.0 ± 4.0	94.1	4.30	0.80	0.085	0.55	0.00
S37	VIII/2	?	71.4 ± 2.4	82.7	38.9 ± 1.3	89.8	9.00	0.45	0.052	0.50	0.00
S38	VIII/2	?	80.6 ± 0.5	91.0	68.3 ± 4.6	94.4	4.55	0.20	0.101	0.55	0.00
S39	VIII/3	Hall (?)	74.4 ± 2.6	86.8	36.5 ± 2.0	92.9	5.30	0.65	0.018	0.75	0.25
S40	VIII/3	Hall (?)	79.9 ± 0.9	92.7	38.9 ± 1.9	94.3	3.95	0.55	0.012	0.90	0.10
S41	IX/1	Hall	73.4 ± 2.0	84.3	41.6 ± 2.6	93.8	4.00	0.55	0.014	0.90	0.50
S42	IX/1	Hall	71.9 ± 3.6	85.9	39.9 ± 2.0	90.1	8.10	0.70	0.010	0.80	0.10
S43	IX/1	Hall	75.0 ± 1.6	90.0	40.6 ± 3.1	90.0	6.80	1.10	0.011	1.30	0.60
S44	IX/2	Hall	72.5 ± 0.2	83.5	41.5 ± 2.3	90.3	8.29	0.48	0.026	0.54	0.20
S45	IX/2	Hall	64.5 ± 1.8	79.6	38.9 ± 2.1	85.5	12.85	0.55	0.013	0.65	0.25
S46	IX/2	Hall	67.7 ± 0.7	83.3	38.1 ± 2.3	83.7	14.60	0.60	0.028	0.70	0.20
S47	IX/2	Hall	76.4 ± 0.6	86.6	35.9 ± 5.0	92.9	5.45	1.15	0.012	0.25	0.05
S48	IX/5	Hall	72.5 ± 1.2	85.1	64.0 ± 2.3	90.4	7.45	0.95	0.017	0.95	0.00
S49	IX/5	Hall	75.4 ± 1.8	82.9	68.2 ± 2.0	89.8	9.60	0.20	0.033	0.20	0.00
S50	IX/5	Hall	69.4 ± 2.9	84.9	35.5 ± 1.4	84.4	13.95	0.75	0.033	0.75	0.00
S51	X/1	Hall	76.7 ± 0.6	86.2	41.2 ± 4.3	93.9	4.75	0.55	0.002	0.65	0.00
S52	X/1	Hall	78.5 ± 2.3	89.6	41.6 ± 3.2	93.7	4.10	1.10	0.000	0.70	0.20
S53	X/1	Hall	73.5 ± 1.8	88.2	43.3 ± 1.6	90.7	6.50	1.40	0.000	0.75	0.45
S54	X/2	Hall	77.0 ± 0.7	85.5	41.1 ± 2.5	94.8	4.15	0.35	0.006	0.45	0.00
S55	X/2	Hall	71.1 ± 1.0	81.1	39.6 ± 2.4	92.4	6.20	0.55	0.003	0.55	0.15
S56	X/2	Hall	75.6 ± 1.9	85.9	38.1 ± 2.7	92.6	6.02	0.61	0.000	0.43	0.14

[a] Take into account that the concentrations given by PIXE and EDXRF represent results mainly from the corroded near-surface regions. The SEM/EDX bulk concentrations were obtained from measurements on cross-sections.

[b] The Ag K/Ag L intensity ratio refers to the value obtained from non-corroded Ag–Cu standards.

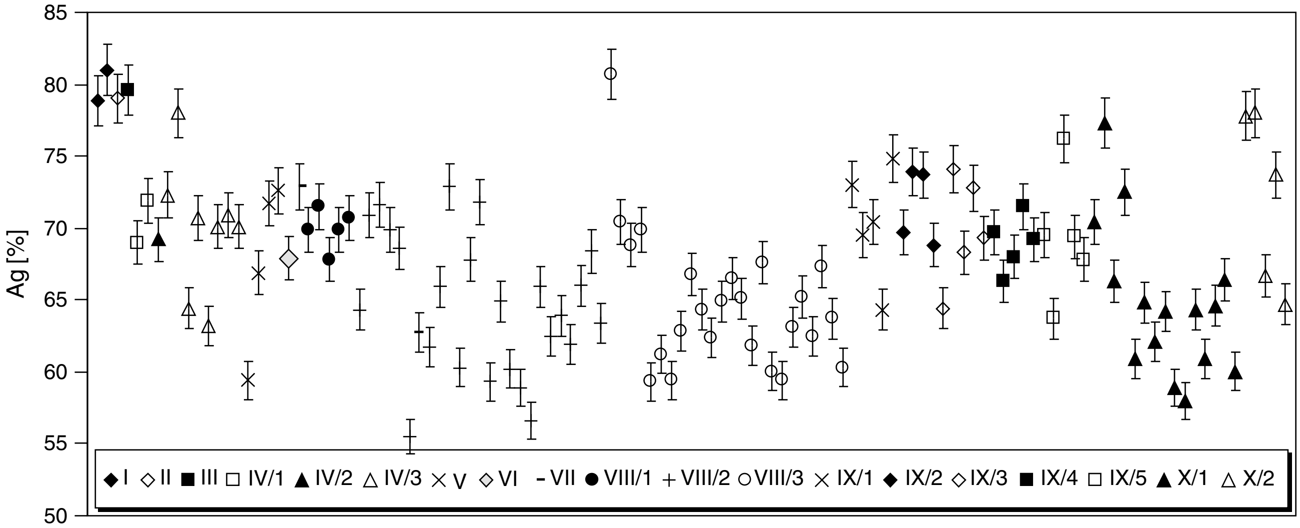

Figure 2. Silver contents of the coins of Archduke Sigismund, measured by EDXRF. The coins are listed in the chronology of mintage. Roman numerals indicate the groups of coinage, Arabic numerals indicate subgroups according to numismatic criteria. The error bars indicate an average deviation between obverse and reverse of 2.2 rel.%.

over an extremely wide range, it has to be assumed that this distribution results from corrosion processes, which modify the initial chemical composition of the near-surface regions.

Apart from copper, all coins contain amounts of lead and bismuth. In a few coins traces of iron, gold, mercury and antimony could also be observed. Figure 3 shows details of the spectra of two coins minted in Merano (S30) and Hall (S53). Coin S53 shows higher x-ray intensities than coin S30 for the elements lead and bismuth but a comparative evaluation of the lead intensities of all coins precluded a significant differentiation. As can be seen in Fig. 4, a comparison of the elements bismuth and gold shows that coins from the mint of Merano partially contain higher amounts of bismuth, whereas coins from the Hall mint contain higher concentrations of gold. However, a clear distinction between the two mints cannot be drawn. Whereas coins of subgroup VIII/1 are similar to coins of groups I–VII (Merano), those of subgroup VIII/3 are similar to those of groups IX and X (Hall). In the scatterplot (Fig. 4), coins of the subgroup VIII/2 are located between the coins of known provenance, which might indicate a continuous succession, but a clear assignment cannot be carried out.

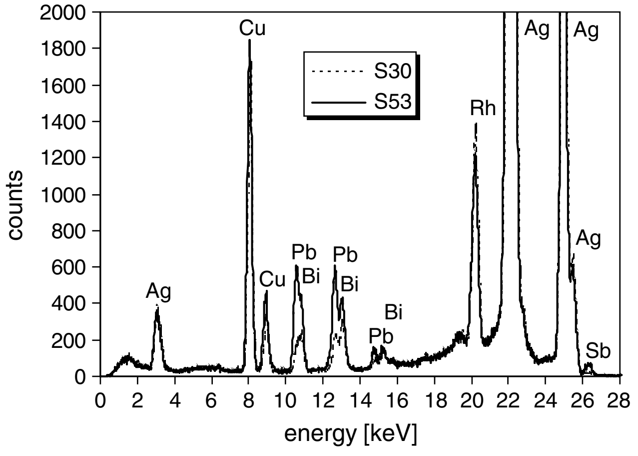

Figure 3. EDXRF spectra of coins from Merano (S30) and Hall (S53). The spectra show differences in the intensities of lead and bismuth, but compared with the PIXE spectra in Fig. 10, no nickel can be observed in the coin S30. The rhodium line stems from the x-ray tube.

In the case of surface-corroded objects, a major disadvantage of EDXRF is its low information depth, which is a function of the energy of both the primary and the fluorescence radiation and also of the chemical composition of the specimen itself. Applied to corroded objects non-destructively, it has to be considered that the results obtained from the surface do not represent the chemical composition of the core. Owing to corrosion processes the base components of the alloy will be oxidized and dissolved. Consequently, the surface of the coin will be depleted of these elements and an enrichment of the noble constituents of the alloy will occur. In the secondary reaction with the constituents of the environment the leached components form corrosion products on the surface of the coins, which have been removed by abrasion during circulation and prior conservation. Therefore, the main question arises of the extent to which the chemical composition in the present state corresponds to that of the time of production.

For silver, both the Ag K and Ag L signals, obtained in the spectrum, allow the evaluation of the depleted layer.[17] Whereas Ag Lα radiation (energy 3.0 keV) originates dominantly from a depth of up to 2 μm, the information depth of the Ag Kα radiation (energy 22.2 keV) is up to ~100 μm in a silver–copper matrix owing to its higher energy. By calculating the ratios of Ag L/Ag K intensities it is possible to obtain information on the degree of depletion. The value of this ratio can be used as an indication of whether silver is enriched at the surface of a coin or not and it can be applied for estimating the error which occurs when EDXRF is used non-destructively. By comparing these results with data obtained from non-corroded and polished silver–copper standards of similar composition, it can be seen that the Ag L/Ag K intensity ratios of the coins are up to ~20% higher, which indicates that silver is enriched at the surfaces of the coins (see Table 1).

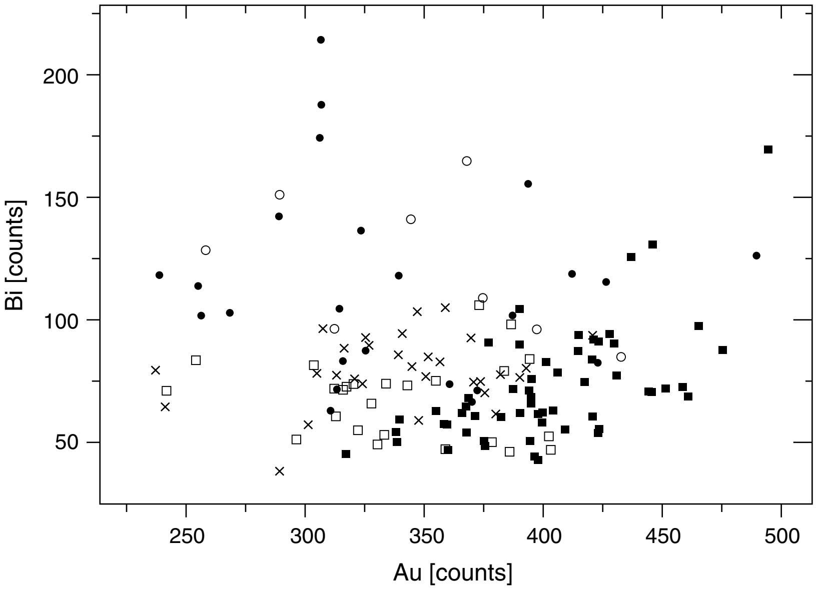

Figure 4. Comparison of the number of observed photons (counts) of the elements bismuth and gold. ●, Coins from the Merano mint; ○, coins for which Merano is supposed to be the mint (group VIII/1); ×, coins of unknown provenance (group VIII/2); □, coins for which Hall is supposed to be mint (group VIII/3); ■, coins from the Hall mint.

Interactions of the photons due to absorption and scattering effects result in a decrease in the intensity of the fluorescence radiation. The thickness D of a layer, which emits 63.2% of the fluorescent intensity of a bulk material of infinite thickness, is given by Eqn (1).[18] This equation applies to the characteristic radiation and neglects secondary or tertiary excitation, which alter the value of D slightly.

$$D = \frac{1}{\rho\left[\dfrac{\mu(E)}{\sin\Psi_1} + \dfrac{\mu(F)}{\sin\Psi_2}\right]} \qquad (1)$$

where

D = thickness of layer, which emits 63.2% of the fluorescent intensity (cm);
ρ = mass density (g cm^{-3});
$\mu(E)$ = mass absorption coefficient of the specimen for the incident photons (cm^2 g^{-1});
$\mu(F)$ = mass absorption coefficient of the specimen for the observed fluorescent photons (cm^2 g^{-1});
Ψ_1 = angle between the primary beam and the specimen surface (in our case 45°);
Ψ_2 = take-off angle between the fluorescent beam and the specimen surface (in our case 45°).

As can be seen in Figure 5, the main portion of the fluorescence radiation originates from the top layer and the total intensity increases following a non-linear function. In silver–copper alloys the thickness of layer D, which emits 63.2% of the silver fluorescent intensity, increases with growing silver content, whereas the corresponding thickness of Cu Kα radiation decreases (Fig. 6). Owing to the lower energy of Cu Kα radiation compared with Ag Kα radiation, the Cu Kα intensity is relatively more affected by absorption effects in the matrix.

Figures 7 and 8 show the influence of the matrix composition on the information depth. Whereas the information depth of Ag Kα radiation in a pure silver matrix is up to ~110 µm (99% intensity), in a nearly pure copper matrix it is only ~65 µm (99% intensity). For Cu Kα, an information depth of ~45 µm can be calculated for pure copper, which decreases in correspondence with the matrix composition (see Fig. 8).

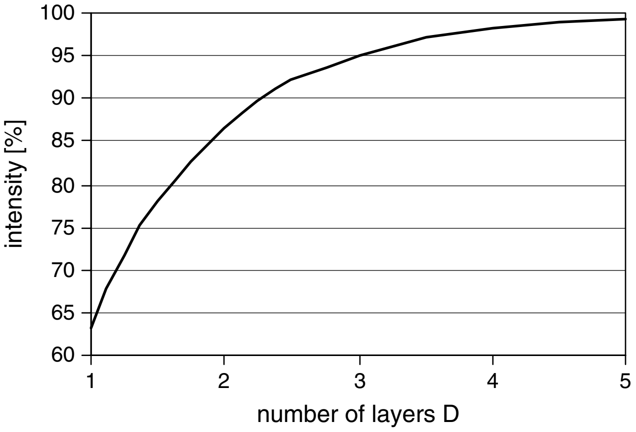

Figure 5. Non-linear increase of the intensity of the fluorescent radiation as a function of the layer thickness.

In order to determine the thickness of the depleted layer and the silver concentration in the (non-corroded) core of the coins, SEM/EDX was applied to cross-sections of a few selected coins, which were in a bad state of preservation anyway.

Scanning electron microscopy

In the backscattered electron image (Fig. 9), the enrichment of silver and the depletion of copper could be observed, which is obviously due to corrosion processes. The dark areas show the copper-rich phase and the bright areas represent the silver-rich phase. The surfaces of the coin

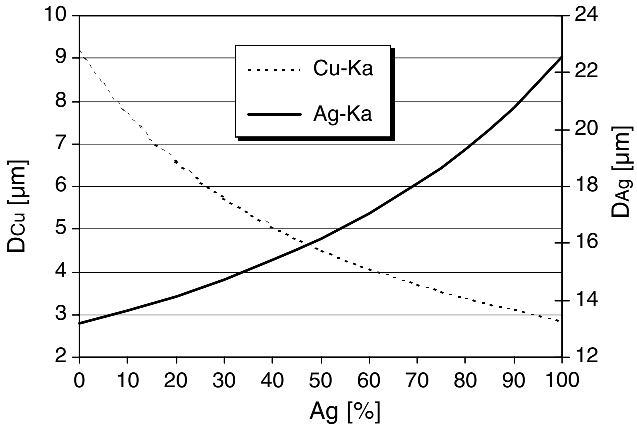

Figure 6. Regarding a silver–copper alloy with increasing silver content, the thickness of the layer D (63.2%) of Ag Kα radiation (D_{Ag}) increases with increasing silver content, while the corresponding thickness of Cu Kα radiation (D_{Cu}) decreases.

show cavities, black in the image between the bright silver-rich phase, which were caused by leaching and diffusion of copper during the corrosion process. The thickness of this surface layer, copper depleted and silver enriched, varies on average between 50 and 200 µm. From Figs 9 and 10, it follows that removal of the corrosion products formed on the coins does not fulfil the requirement for a quantitative analysis of the alloy as the corrosion affects parts of the coin invisible to the naked eye. As the information depth of SEM/EDX is only 1–5 µm, it has to be considered that SEM/EDX investigations, carried out on the surfaces of the coins without sampling, would not have been successful in this case. Although all coins had been buried under the same conditions and for the same time, they show different stages of corrosion. Therefore, in SEM on the cross-sections both completely depleted coins and objects with a leached layer of just a few micrometres could be observed. The concentrations of silver range from 35.3 ± 1.5 to 76.0 ± 1.6% (see Table 1). The standard deviations vary in the range 0.8–6.9% due to an inhomogeneous elemental distribution and depending on the domain selected on the cross-section for the analysis. No trace elements could be detected owing to the high background of the bremsstrahlung induced by the electron bombardment.

It has to be considered that apart from corrosion occurring in air and wet soil, leaching phenomena can also be caused by chemical treatments of an object. Organic or inorganic acidic solutions dissolve the base constituents of the alloy, while the more noble components, e.g. silver or gold, are enriched at the surface. These methods of blanching artefacts made of silver and gold alloys have partially been applied since ancient periods in order to give the objects more brightness and glimmer.[19,20] However, no hints could be found in the archives that the 'Tiroler Kreuzer' was treated in such a way. Owing to the bad state of preservation and the corrosion processes observed, no distinction could be made as to whether the coins were depleted by blanching or due to corrosion effects. Because blanching techniques usually do not exceed a depth of a few micrometres, corrosion processes would superimpose any blanching layer.

Comparing the quantitative results obtained by EDXRF and SEM/EDX, the silver concentrations obtained by SEM/EDX at the cross-sections in the non-corroded core of the coins are lower than those determined by EDXRF. The differences range from 3.2 to 105.4 rel.%. The SEM investigations clearly demonstrate that quantitative bulk analysis via non-destructive EDXRF is impossible, as the thickness of the leached layer is usually equivalent to the depth of the fluorescence radiation of the Ag Kα line or even partially exceeds it.

For conservation reasons, only a limited number of coins could be cross-sectioned for research work. Because SEM/EDX was not able to determine minor and trace elements for additional characterization of the mints, it was decided to study the coins with regard to trace elements by means of non-destructive external PIXE.

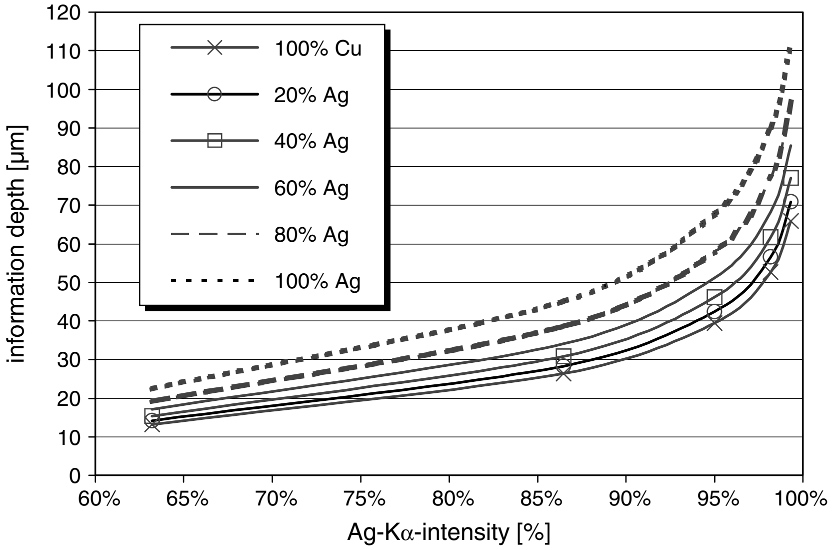

Figure 7. Increase in the information depth of Ag Kα radiation in silver–copper alloys of varying compositions depending on the thickness of the layer.

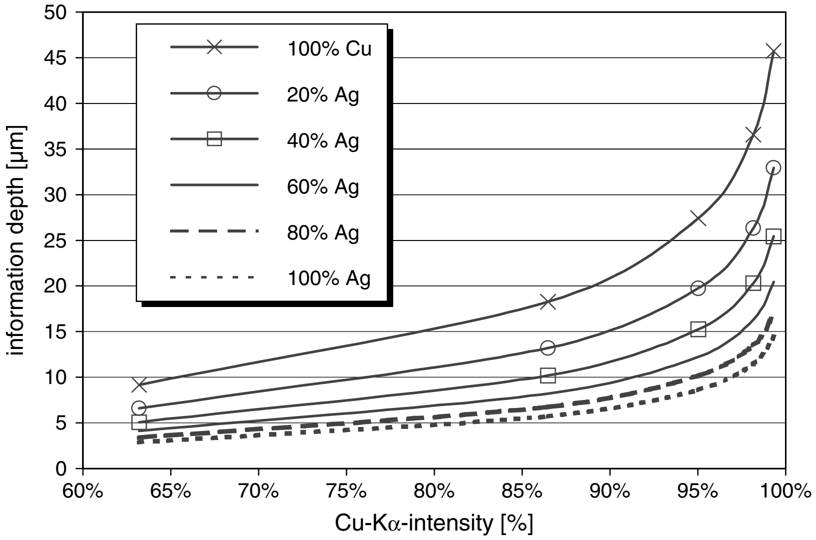

Figure 8. Increase in the information depth of Cu Kα radiation in silver–copper alloys of varying compositions depending on the thickness of the layer.

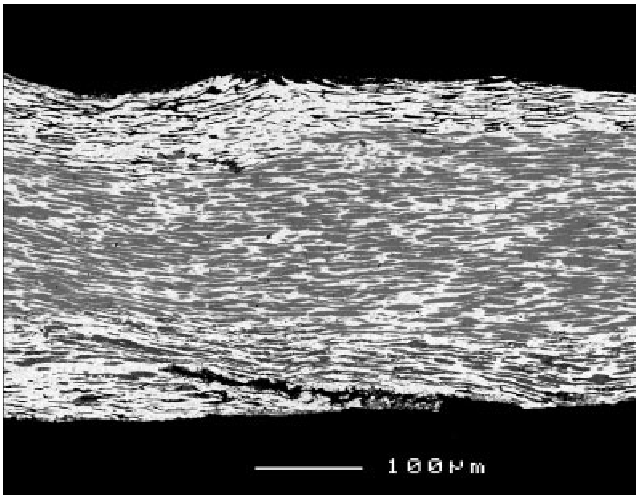

Figure 9. Backscattered electron image of a cross-section of a 'Tiroler Kreuzer.' The bright areas indicate the silver-rich and the dark areas the copper-rich phase of the alloy. An enrichment of silver and brittle areas due to corrosion can be seen on the two surfaces of the coin. Owing to diffusion of copper, cavities are formed within a range of ~50 µm.

Proton-induced x-ray emission with external beam

At present, PIXE probably represents the most popular ion beam technique for non-destructive analysis of archaeological artefacts.[21] Compared with other techniques, the information depth of PIXE in metal (up to ~5–10 µm) exceeds that of SEM/EDX (up to ~1–5 µm) slightly, but is clearly lower compared with XRF (up to ~100 µm). As the analyses carried out so far with SEM have found that the depth of the corroded layer ranges from 50 to 200 µm, it has to be considered that under these circumstances non-destructive PIXE is not suitable for the determination of silver bulk concentrations of the coins. On the other hand, as only very low bremsstrahlung is induced by the protons, this technique permits lower detection limits of the elements compared with EDXRF and SEM/EDX.

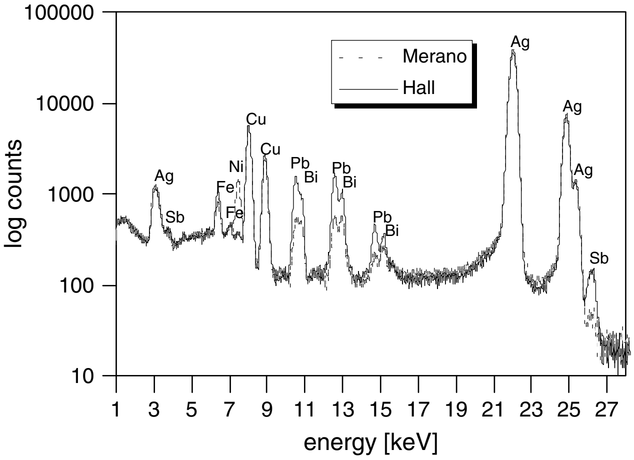

Figure 10. PIXE spectra of coins from Merano (S30) and Hall (S53). Apart from differences in the intensities of lead and bismuth, the coin S53 contains no nickel, whereas in the coin S30 this element could be clearly observed.

The elements silver, copper, lead, bismuth and iron were detected in all coins, and several coins also contained traces of nickel, antimony, gold and mercury. Quantitative evaluation took into account the elements silver (mean ± SD 91.4 ± 2.8%), copper (6.8 ± 2.9%), lead (0.7 ± 0.3%), bismuth (0.6 ± 0.3%), antimony (0.2 ± 0.2%) and nickel (0.03 ± 0.03%).

Figure 10 shows the spectra of two coins from the mints of Merano (S30) and Hall (S53). In contrast to the spectra acquired for the same coins by means of EDXRF (Fig. 3), traces (0.068%) of nickel could be detected in the coin S30. Nickel could not be detected in the EDXRF spectrum. Compared with XRF and SEM/EDX, the results for silver show higher values owing to the depleted surface layer and the low penetration depth of the protons (Table 1). The evaluation of the trace and minor components indicates that only the elements nickel and bismuth allow a distinction between coins minted in Merano and Hall (Fig. 11).

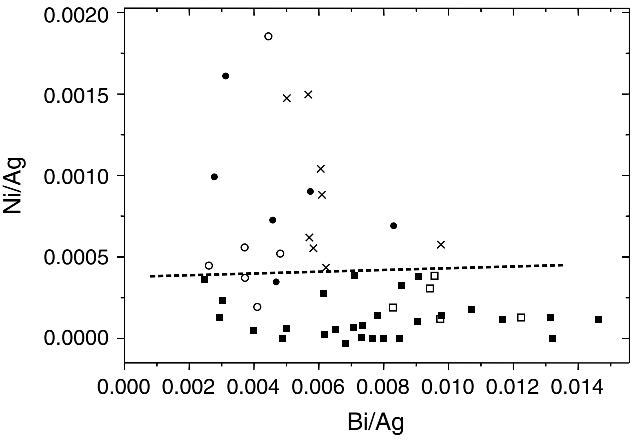

Figure 11. Comparison of Ni/Ag and Bi/Ag concentration ratios as present within the corrosion layer. ●, Coins from the Merano mint; ○, coins for which Merano is supposed to be the mint (group VIII/1); ×, coins of unknown provenance (group VIII/2); □, coins for which Hall is supposed to be the mint (group VIII/3); ■, coins from the Hall mint.

The comparison of the Ni/Ag and Bi/Ag concentration ratios shows that most coins minted in Merano contain higher amounts of nickel whereas the majority of those minted in Hall are characterized by higher concentrations of bismuth. According to this finding, coins of subgroups VIII/1 and VIII/2 can be related to the mint of Merano. Coins of subgroup VIII/3 are more similar to the mint of Hall according to their concentrations of nickel and bismuth.

In conclusion, it has been shown by means of PIXE that the subgroups VIII/1 and VIII/3 were minted in Merano and Hall, respectively, as initially suggested by numismatists. The similarity of the chemical composition of coins of subgroup VIII/2 with coins of the mint of Merano can be interpreted as evidence for a change of the mint between subgroups VIII/2 and VIII/3. Although PIXE does not characterize the bulk material of the coins, the results show clear differences in the nickel concentrations between the two mints. As all coins were buried for the same period in one jar, nickel enrichment of the coins of Merano from soil can be excluded.

CONCLUSION

Determining the chemical composition of late medieval silver–copper coins, it has been shown that even if the objects are corroded, it is possible to obtain chemical information that allows an interpretation of the geographical origin. Whereas at the beginning it was intended to perform the analyses non-destructively by EDXRF, the results show that this technique is limited, mainly if applied quantitatively, if the thickness of the leached surface layer exceeds the information depth of the x-radiation. Calculating the ratios of x-ray intensities of Ag Kα and Ag L radiation an enrichment of silver in the surface layer of the coins could be demonstrated without any damage. In order to determine the silver concentration of the coins, investigations were carried out on cross-sections of the coins by SEM/EDX. The analyses, which were carried out on coin fragments or coins that were already in a bad state of preservation, show a depleted layer of 50–200 μm. Compared with EDXRF, SEM/EDX investigations carried out at cross-sections in the non-corroded core of the coins show lower silver concentrations. The EDX detector in the SEM precluded the detection of elements different from silver and copper owing to the background of the electron bremsstrahlung. Therefore, no data could be obtained regarding the provenance of the coins. Finally, PIXE was applied in order to detect elements in the low concentration range non-destructively. Although PIXE was not suitable for determining silver concentrations of the coins' bulk non-destructively, owing to its low information depth, the lack of primary electron bremsstrahlung was advantageous for detecting elements at low concentration levels. The results show that by determining the nickel and bismuth contents of the coins, distinctive marks could be defined concerning the question of provenance.

Acknowledgement

PIXE measurements were carried out at the Laboratoire d'Analyses par Réactions Nucléaires (LARN) in Namur (Belgium) within a short-term scientific mission of the COST (European Cooperation in the Field of Scientific and Technical Research) G1 collaborative programme.

REFERENCES

1. Alram M, Winter H, Metlich M. *Numismat. Z.* 1997; **104/105**: 109–185.
2. Wieser F. *Numismat. Z.* 1965; **81**: 14–20.
3. Rizzolli H. *Beiträge zur Wirtschaftsgeschichte Südtirols. Festschrift zum 125jährigen Bestehen der Südtiroler Sparkasse*. Bozen, 1979; 359–455.
4. Linke R, Schreiner M. In *Die Frühzeit des Friesacher Pfennigs*, Alram M, Härtel R, Schreiner M (eds). Osterreichische Akademie der Wissenschaften: Vienna, 2002; 467–513.
5. Mantler M, Schreiner M. *X-Ray Spectrom.* 2000; **29**: 3–17.
6. Carlson JH. *MASCA Res. Pap. Sci. Archaeol.* 1989; **6**: 73–81.
7. Klockenkämper R, Becker M, Otto H. *Spectrochim. Acta, Part B* 1990; **45**: 1043–1051.
8. Love LJC, Soto L, Reagor BT. *Appl. Spectrosc.* 1980; **34**: 131–139.
9. Stern WB. In *Methoden zur Erhaltung von Kulturgütern*, Schweizer F, Villiger V (eds). Haupt: Berne, 1989; 181–192.
10. Barrandon JN, Callu JP, Brenot C. *Archaeometry* 1977; **19**: 173–186.
11. Meyer M-A, Demortier G. *Nucl. Instrum. Methods Phys. Res. B* 1990; **49**: 300–304.
12. Beauchesne F, Barrandon JN, Alves L, Gil FB, Guerra MF. *Archaeometry* 1988; **30**: 187–197.
13. Demortier G, Morciaux Y. *Nucl. Instrum. Methods Phys. Res. B* 1994; **85**: 112–117.
14. Van Oystaeyen B, Demortier G. *Nucl. Instrum. Methods* 1983; **215**: 299–313.
15. Demortier G, Mathot S, Van Oystaeyen B. *Nucl. Instr. Meth. Phys. Res.* 1990; **B 49**: 46–51.
16. Linke R, Alram M, Martinek K-P, Demortier G, Spindler P, Schreiner M. *Numismati. Z.* 2001; **108/109**: 125–149.
17. Linke R, Schreiner M. *Mikrochim. Acta* 2000; **133**: 165–170.
18. Mantler M, Schreiner M. *X-Ray Spectrom.* 2000; **29**: 3–17.
19. Zwicky-Sobczyk CN, Stern WB. *Archaeometry* 1997; **39**: 393–405.
20. Klockenkämper R. *Fresenius'. Z. Anal. Chem.* 1978; **290**: 212–216.
21. Demortier G. *Nucl. Instrum. Methods Phys. Res. B* 1992; **64**: 481–487.