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The sixteenth-century glass jewellery collection of Archduke Ferdinand II – a great challenge for semi-quantitative XRF investigations

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KK_2792

Introduction

The glass jewellery collection of Archduke Ferdinand II, now on display in the Collection of Sculpture and Decorative Arts (Kunstkammer) of the Kunsthistorisches Museum Vienna, is very unique in many ways. First of all, it is a rare example of a bigger collection of early modern lampworked glass. Secondly, although it was produced at the glasshouse of the Innsbruck ducal court, operating between 1570 and 1591, Venetian glassblowers were engaged for limited periods, bringing with them the whole material needed for the production of these outstanding fragile works of art. Considering the conservation state 32 objects could be analysed with the aim of achieving semi-quantitative results for description and comparison of the glass materials used.

Method and problem statement

In the course of the examination of this collection X-ray fluorescence (XRF) analysis, using the self-constructed PART II (Portable Art Analyser) system, was performed. This method was chosen because of its non-destructiveness and the non-portability of the objects. Nevertheless, analysing glass using XRF has to cope with some general problems:

- Absorption of the radiation of light elements (especially Na) in air - although the air path is only about 1 mm using the PART II
- Corrosion of glass-surfaces, leading to a depletion of Na (visible on several items of the collection, especially some hues of blue)

Regarding the glass jewellery collection there were additional problems:

- Extremely varying thicknesses of the glass parts
- Complex shapes of the objects, complicating the access for analysis

Comparative measurements on fragments not assignable to specific items could be carried out using SEM/EDX* (energy dispersive microanalysis in a scanning electron microscope).

Approaches

For the evaluation of the XRF data two software packages were available:

- XRS-PF of Amptek:
  It showed difficulties when Ca was evaluated in the presence of Sn, leading to an extreme overestimation of Ca. As the opacifier in all opaque glasses is PbO and SnO_2 this program was not suitable for the analysis of the glass jewellery items.
- WinAxil of Canberra:
  Here all components could be evaluated semi-quantitatively by using "Compare Mode".
  The calculation cannot be done in the form of oxides – the conversion has to be done in an additional step using Excel, complicated by the output format of the program (both % and ppm is used). ➡ Method of choice

⬇

- Evaluation showed that, although surfaces without visible corrosion were chosen, a depletion of Na was present.
- For thin glasses the sum of analysed elements was much less than 100 %.

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- ✓ normalisation is necessary
- ✓ Na leads to the highest uncertainty and is neglected for normalisation

Conclusions

Quantitative analysis of items like the glass jewellery collection of Archduke Ferdinand II is not possible using portable XRF in situ. Nevertheless, to be able to compare the different glass parts and colours a semi-quantitative approach was successfully applied. Glass types could be identified with a higher certainty than with earlier approaches** and specific characteristics of different glass parts specified.

The results of SEM/EDX and XRF are in good accordance although SEM/EDX could only be performed on not assignable fragments.

Further studies of the results may lead to characteristic groupings of the items, according to the craftsman creating them.

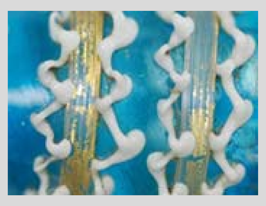
* SEM/EDX measurements were performed at:
- Vienna University of Technology, Institute of Chemical Technologies and Analytics, Austria, with a Quanta 200 MK2 instrument equipped with an EDX-detector of AMETEK (detector type: Super UTW Sapphire)
- LAMA, Università IUAV di Venezia, Italy, with a Philips XL30 instrument equipped with an EDAX XL30 X-ray microanalyser and EPMA with a microprobe Cameca SX-50 equipped with three wavelength-dispersive spectrometers and PET, LiF, and TAP crystals

Results

The examples shown will focus on colourless and blue glass. Blue glass existed in several different hues. Three of them could be investigated using SEM/EDX and XRF.


'blue 1' transparent


'blue 2' transparent


'blue 3' transparent


'colourless' transparent

SEM/EDX

The elaborated method could be tested on the SEM/EDX results of real samples and proofed to provide valuable information concerning glass type, colouring elements and comparison of the samples.

Sample	Color	Na_2O	MgO	Al_2O_3	SiO_2	P2O5	SO_3	Cl	K_2O	CaO	MnO	Fe_2O_3	CoO	CuO	ZnO	PbO	Sum [%]	Glass Type
KHM-7	b1	9,6	2,6	2,2	69,4			0,5	6,7	6,3	1,1	1,6					100	Mixed Alkali
KHM 31	b1	9,5	2,8	2,1	69,4	0,4	0,3	0,5	6,3	6,2	0,8	1,3	0,4				100	Mixed Alkali
KHM 32	b1	11,7	3,1	1,5	68,3	0,2	0,3	0,8	2,3	9,8	0,5	1,2				0,4	100	Mixed Alkali
KHM 34	b2	8,4	3,3	1,4	69,0	0,2	0,9	0,6	2,7	4,6	0,7	3,8		1,0	1,4	2,1	100	Soda-lime-silica
KHM-10	b3	9,9	0,3	1,0	78,5		0,8	1,6	3,3	0,9		0,7		2,9			100	Cristallo
KHM 35	b3	4,2	0,6	1,4	83,9	0,2	0,6	1,5	2,0	1,4	0,3	0,8		2,9		0,4	100	Cristallo
KHM-3	c	12,0	3,1	1,4	65,5			1,0	4,7	10,2	0,8	0,9					100	Soda-lime-silica
KHM 22	c	10,5	3,0	1,1	67,0		0,4	0,8	4,8	11,1	0,6	0,5					100	Soda-lime-silica
KHM 23	c	10,7	3,0	1,2	68,9	0,3	0,2	0,7	5,8	8,2	0,5	0,7					100	Soda-lime-silica

Results [in wt%] obtained with SEM/EDX on fragments – elements that are important for glass and colour identification are indicated in red

Sample	Color	Na_2O	MgO	Al_2O_3	SiO_2	P2O5	SO_3	Cl	K_2O	CaO	MnO	Fe_2O_3	CoO	CuO	ZnO	PbO	Sum [%]	Glass Type
KHM-7	b1		2,9	2,4	76,8			0,6	7,4	7,0	1,2	1,8					100	Mixed Alkali
KHM 31	b1		3,1	2,3	76,7	0,4	0,4	0,6	7,0	6,8	0,9	1,5	0,4				100	Mixed Alkali
KHM 32	b1		3,5	1,7	77,4	0,2	0,4	0,9	2,6	11,1	0,5	1,3				0,4	100	Mixed Alkali
KHM 34	b2		3,6	1,6	75,4	0,2	1,0	0,6	2,9	5,0	0,7	4,1		1,0	1,5	2,3	100	Soda-lime-silica
KHM-10	b3		0,3	1,1	87,1		0,8	1,7	3,7	1,0		0,8		3,3			100	Cristallo
KHM 35	b3		0,6	1,4	87,6	0,2	0,6	1,6	2,1	1,4	0,3	0,8		3,0		0,4	100	Cristallo
KHM-3	c		3,6	1,6	74,7			1,2	5,3	11,6	0,9	1,0					100	Soda-lime-silica
KHM 22	c		3,4	1,2	75,0		0,5	0,9	5,4	12,4	0,7	0,6					100	Soda-lime-silica
KHM 23	c		3,4	1,3	77,1	0,3	0,2	0,8	6,5	9,1	0,5	0,7					100	Soda-lime-silica

Results [in wt%] obtained with SEM/EDX on fragments – normalised disregarding Na; the main components for classification show still characteristic relations

XRF

	Color	MgO	Al_2O_3	SiO_2	P_2O_5	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	NiO	CuO	ZnO	As_2O_3	SrO_2	BaO	PbO	Bi_2O_3	Glass Type	Coloring elements
KK_2681	b1	5,9	2,1	71,1	0,3	0,8	5	10,6	0,1	1,2	1	0,3	0,2	0,1	0,05	0,5	0,1		0,7	0,2	Soda-lime-silica	Co
KK_2797	b1	3	2,2	77,4	0,3	1	2,5	11,3	0,1	*	0,8	0,2	0,1	0,2	*	0,5	0,2		*	0,4	Soda-lime-silica	Co
KK_2875	b1	2,3	3,1	73,6	0,7	0,3	9,1	7,5	0,1	0,9	1,4	0,1	*	*	*	0,2	0,1	0,1	0,1	0,1	Mixed Alkali	Co
KK_3011	b1	2,2	2,9	76	0,6	0,3	8,6	6,7	0,1	0,8	1	0,1	*	*	*	0,2	0,1	0,1	0,1	0,1	Mixed Alkali	Co
KK_3041	b1	3,2	2,1	73,8	0,5	0,4	9,5	7,2	0,2	1,1	1,4	0,2	*	*	0,1		0,1	0,2	0,1	0,1	Mixed Alkali	Co
KK_2680	b2	0,6	1,2	86,2	0,2	0,8	3,9	1,4	0,05	0,1	0,4			4,9			*		0,3		Cristallo	Cu
KK_2777	b2	4,5	0,9	85,3		0,5	2,8	0,9	*	0,2	0,3	*	*	4,3			*		0,3		Cristallo	Cu
KK_2792	b2	0,3	1,3	88,7	0,1		2,7	1,6	*	0,1	0,3		*	3,7			*		1,3		Cristallo	Cu
KK_2796	b2	0,1	2,3	91,2	0,1	0,3	2,5	0,5	*	*	0,3	*	*	2,3	*	0,1	*		0,1	*	Cristallo	Cu
KK_2828	b2	2,4	1,8	80,9	0,4	0,8	2,7	7,3	0,1	0,4	0,4	*	*	2,5		0,1	*		0,2		Soda-lime-silica	Cu
KK_2681	b3	1,5	1,5	84,4	0,2	1,6	2,8	2,6	0,1	0,1	0,9			3,7	0,1		*		0,6		Cristallo	Cu
KK_2741	b3		1,2	84,7	0,3	0,9	3,3	1,6	0,1	0,1	0,6		*	4,9			0,05		2,4		Cristallo	Cu
KK_2800	b3	2,7	1,2	73,4	0,2	1	4	13,2	0,1	0,3	0,7			2,6			*		0,6		Soda-Kalk	Cu
KK_2865	b3	1,7	1,3	86,7	0,3	0,3	3,8	2,3	*	*	0,3			3,1	*		*		0,2		Cristallo	Cu
KK_2921	b3	4,8	1,4	83,9	0,2	0,8	2,9	1,2	*	*	0,4		*	3,8		0,2	*		0,3		Cristallo	Cu
KK_2680	c	3,5	1,9	70,9	0,8	1,7	5,6	13,9	0,3	0,4	0,7			0,1			0,2		0,2		Soda-lime-silica	
KK_2681	c	2,6	1,8	74,6	0,2	1,1	7	10,6	0,1	1,1	0,7			*	*		0,1		0,1		Soda-lime-silica	
KK_2681	c	5,6	1,9	74,2	0,3	1,5	2,7	12,4	0,1	0,6	0,7			*	*		0,1		0,1		Soda-lime-silica	
KK_2699	c	2,9	1,9	76,5	0,3	0,9	5,7	10,7	*	0,3	0,4			*			0,1		0,1		Soda-lime-silica	
KK_3041	c	3	1,3	74,7	0,3	0,9	9,2	9,4	0,1	0,4	0,4			*			0,1		0,1		Mixed Alkali	

Results [in wt%] obtained with XRF – normalised disregarding Na; trace elements < 500 ppm are indicated with *

The differently coloured glasses posses characteristic properties. 'Blue 1' glass exists either as soda-lime glass or mixed alkali glass, Co is the colouring element. The 'blue 2' glass is mainly cristallo. For 'blue 3' cristallo and soda-lime-silica glass can be found. For the 'blue 2' and 'blue 3' glass Cu is responsible for the colour, in 'blue 3' there seems to be a little more Fe.

All analysed colourless glasses are of soda-lime silica glass with the exception of KK_3041:
There the colourless glass is mixed alkali. The 'blue 1' glass is again mixed alkali and the 'green 2' glass is the only potash-lime-silica glass that could be found in all the items. The whole item is conspicuous concerning its workmanship and has to be reconsidered in the context of the collection.


KK_3041

** Literature:
E. Putzgruber, M. Verità, K. Uhlir, B. Frühmann, M. Grießer, G. Krist, *Scientific investigation and study of the sixteenth-century glass jewelry collection of Archduke Ferdinand II*, in *2012 Vienna Congress, The Decorative: Conservation and the Applied Arts*, IIC Vienna Congress 10. -14. September 2012, Studies in Conservation 57/1, S217 - S226

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