Hispano-Moresque tiles in Portugal

The collections of *Palácio Nacional de Sintra* and *Mosteiro de Santa Clara-a-Velha* in Coimbra

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In memoriam of our dear friend and colleague Vânia S.F. Muralha

This paper examines Hispano-Moresque glazed tiles (15th-16th century) from the collections of Palácio Nacional de Sintra and Mosteiro de Santa Clara-a-Velha, in Portugal. A representative number of tiles from the two collections was analysed by µ-PIXE (particle induced X-ray emission), SEM-EDS (scanning electron microscopy with X-ray microanalysis) and µ-Raman spectrometry, in order to characterise each collection both chemically and morphologically. This study is included on a wider project concerning the characterisation of Portuguese and Spanish medieval tiles and their provenance.

Introduction

The use of ceramic tiles has been intrinsically connected with Portuguese architecture since the 15th century. Tiles were used to decorate pavements in Portuguese churches from the 13th century, but it was during the reign of King D. Manuel I (r. 1469–1521) that considerable numbers of tiles were used to decorate both noble and religious buildings throughout the country (Trindade 2008). By then, the taste for Hispano-Moresque ceramics was at its peak. Lead-glazed ceramics (including tin-opacified and lustre-decorated ceramics) were developed in several important production centres in the Iberian Peninsula after the Christian *Reconquista*, first by Muslims who remained in the Iberian territory, and later by Christian artisans who learned the technology and adapted it to new decorative patterns (Martinez Caviró 1996).

The decoration techniques also evolved: from the *alicatado*, where flat monochromatic small fragments were put together to form complex geometric patterns, to the *cuerda-seca* technique, where different coloured glazes could be applied on the same ceramic surface, separated by grooves that were filled with a greasy substance mixed with manganese oxide (dark contours separate colours). Later, the *arista* technique once again simplified the process: the colours were then separated by raised contours obtained by pressing the ceramic paste onto a mould. Relief tiles were already used by Islamic communities and were occasionally produced by Hispano-Moresque workshops as well (Martinez Caviró 1996; Trindade 2008).

Hispano-Moresque tiles in Portuguese architecture have typically been considered to have been imported from Spanish production centres, namely Seville, which by then was the main production centre in the Iberian Peninsula. There are written records of Sevillian tiles arriving at Portuguese cities, such as Coimbra and Sesimbra (Trindade 2008). However, other important production centres existed, both in Spain and in Portugal, which challenges the idea that all Hispano-Moresque tiles in Portugal came from Seville (see Alho *et al.* this volume). Also, archaeological evidence shows that, *arista* tiles were made in Santo António da Charneca, on the south shore of the Tagus river

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Figure 1. Examples of samples included in the study, illustrating various decorative techniques. (Image: Authors).

(Trindade 2008; Vieira Ferreira *et al.* 2014). This is reinforced by documentation on Portuguese ceramic production centres (Trindade 2008) and other archaeological evidence, such as trivets (kiln furniture) that were found in the *Palácio Nacional de Sintra* and in the *Mosteiro de Santa Clara-a-Velha* in Coimbra, and unglazed tiles that were also found in Coimbra.

This study focuses on the analytical characterisation of the tiles in order to obtain information on the production technology and pictorial techniques. A representative number of tiles from each of the two collections was analysed by µ-PIXE (particle induced X-ray emission), SEM-EDS (scanning electron microscopy with X-ray microanalysis) and µ-Raman spectrometry, in order to characterise each collection both chemically and morphologically. This study is part of a wider project that aims to characterise Hispano-Moresque tiles from Portuguese and Spanish collections and assess geographical and chronological variation.

The collection of Palácio Nacional de Sintra

The *Palácio Nacional de Sintra* (PNS), or Sintra's National Palace, underwent major expansion work during the reign of King Manuel I. This Palace is often referred to as having one of the most important Hispano-Moresque tile collections in the country. Its walls display a great variety of well-known decorative patterns, both in *cuerda-seca* and *arista* techniques. It also has some unique patterns that have not yet been identified anywhere else in the world, such as the relief tiles with wine-related motifs illustrated in Fig. 1 (Trindade 2008). The PNS relief tiles show different production techniques that suggest different production periods, or a sequence that was necessary in order to "master" the technique from low relief to high-relief. Fig. 1 illustrates two examples of relief tiles from Sintra.

The collection of Mosteiro de Santa Clara-a-Velha (Coimbra)

Founded in 1286, the *Mosteiro de Santa Clara-a-Velha* (SCV), in Coimbra (translated as Monastery of Saint Clare "the Old") is today an archaeological site. The monastery was founded on the bank of the Mondego River and was abandoned in the 17th century due to constant floods. A new monastery was built on higher ground nearby (*Mosteiro de Santa Clara-a-Nova*). The site was excavated in the 1990s and 2000s and a varied collection of Hispano-Moresque tiles was discovered, along with impressive collections of glass and ceramics (Côrte-Real *et al.* 2010).

The excavated tiles feature a range of decorative techniques, with flat tiles, *cuerda-seca* and *arista* tiles, and tiles featuring a star-shaped relief pattern that once formed a part of the decoration of the church ceiling. The decorative motifs demonstrate a wide range of influences, from the Islamic-type geometric patterns to the more complex Renaissance ones. Additionally the collection included unglazed *arista* tiles and hundreds of trivets used to support ceramic objects in the kiln, which attests to the importance of Coimbra as one of the most important ceramic production centres in Portugal at that time (Trindade 2008; Côrte-Real *et al.* 2010). Fig. 1 illustrates one *cuerda-seca* tile and one *arista* tile from the SCV collection. In order to characterise these tiles they were subjected to scientific analysis as described here.

Experimental procedure

Samples

Cross-section samples (1-3 mm wide) from the PNS were collected and mounted in epoxy resin (®Araldite 2020). Finally, the samples were polished in MicroMesh® sheets up to grit 4000. The data were compared with those (prepared in the same way) from our previous publication on the SCV (Coentro *et al.* 2014). Table 1 summarises the number of samples taken and the representation of different decorative techniques in the sample from each collection.

Table 1. Number of studied samples from each collection divided by decoration technique.

Collection	Decoration				Total
	Flat	*Cuerda-seca*	*Arista*	Relief	
PNS	1	7	6	5	19
SCV	1	5	7	1	14

Analytical techniques

Micro Particle Induced X-Ray Emission (μ-PIXE) was performed using an Oxford Microbeams OM150 type scanning microprobe for focusing down a 1 MeV proton beam to 3 x 4 μm^2. The sample fragments were irradiated in a vacuum and the collected X-rays used to obtain 2D elemental distribution maps (typical dimensions of 750 x 750 μm^2). The glaze and the ceramic body of the tiles could be properly identified and a representative region of interest selected for quantitative analysis. Operation and basic data manipulation was achieved through the OMDAQ software code (Grime and Dawson 1995), while quantitative analysis was performed with the GUPIX code (Campbell *et al.* 2010).

Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM-EDS) was undertaken using a HITACHI S-3700N electron microscope with a Bruker Xflash 5010 SDD energy dispersive X-ray (EDX) detector. All samples were observed and analysed in a vacuum atmosphere. The backscattering mode was used for SEM imaging. The resolution of the EDX detector is 123 eV in the Mn Ka line. The system allows reliable chemical point analysis and mapping from Na X-ray emission energy. In order to collect X-ray emissions from heavier elements like lead (Pb), an acceleration voltage of 20 kV was chosen. The EDX tasks and the quantification were achieved through the Esprit1.9 software from Bruker Company.

μ-Raman: Analyses were performed with a Labram 300 Jobin Yvon spectrometer, equipped with a HeeNe laser of 17 mW power operating at 632.8 nm and a solid state laser of 500 mW power operating at 532 nm. The laser beam was focused either with a 50x or a 100x Olympus objective lens. The laser energy was filtered at 10% using a neutral density filter for all analyses. Analyses were performed both on the surface of the glazes and on polished cross-sections. Spectra were recorded as an extended scan. A mixed Gaussian-Lorentzian curve-fit using the LabSpec software was used to determine the exact peak wavenumbers. The attribution of the Raman spectra was made using the RRUFF mineralogical database (http://rruff.info/).

Glaze technology in Hispano-Moresque tiles

Hispano-Moresque tiles are decorated with transparent and tin-opacified lead glazes, consistent with the Islamic technology that was introduced following the Islamic conquest of the Iberian Peninsula. As pointed out by Tite *et al.* (1998), lead glazes show a greater optical brilliance than alkaline glazes, are less prone to crazing due to their lower thermal expansion and are easier to prepare and apply as frits (lead oxide is insoluble in water). Additionally, the natural abundance of galena (PbS) in the Iberian Peninsula promoted the development of many ceramic centres that developed this lead-glaze technology (Molera *et al.* 2001b).

Glaze composition

Silica (SiO_2) and lead oxide (PbO) are the major constituents of Hispano-Moresque glazes. Together, they account for *c.* 75–90wt.% of the total composition, with lower proportions when tin is present. Tin-opacified glazes show lower PbO / SiO_2 ratios. Table 2 summarises the results of the quantitative analysis of the glazes by μ-PIXE.

Tin oxide is the third major constituent in white and blue glazes. It is also the main distinguishing factor amongst these collections. The blue and white glazes from the SCV collection have a higher SnO_2 content (*c.* 7–14 wt%) than the PNS tiles (<9 wt%). This difference is illustrated in Fig. 2, where the PNS

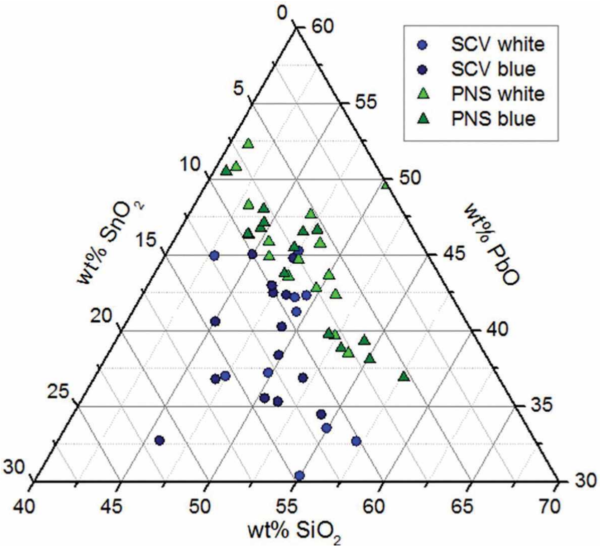


Figure 2. Ternary plot of SiO_2 vs. SnO_2 vs. PbO of white and blue glazes (results obtained by μ-PIXE). (Image: Authors).

Table 2. Chemical composition of the glazes, divided by colours, in wt.% average, obtained by µ-PIXE.

		Na_2O	MgO	Al_2O_3	SiO_2	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	NiO	CuO	As_2O_5	SnO_2	BaO	PbO	Bi_2O_3
White	SCV 10ef175	2,40	0,83	3,10	42,0	0,32	2,48	4,06	0,20	0,05	0,93			0,64		7,02		36,0	
	SCV 10DF7637	1,82	1,20	2,54	41,6	0,23	1,86	3,18	0,19		0,92			0,25		13,68		32,5	
	SCV 20i2989	1,90	0,91	2,34	38,4	0,30	1,95	2,05	0,09		0,72			0,13		10,95		40,3	
	SCV 27i3426	1,99	0,87	1,84	42,5	0,29	1,97	2,51	0,13		0,70			0,12		6,49		40,6	
	SCV 30F7756	2,23	0,77	2,19	47,9	0,25	4,29	2,24	0,14	0,05	0,48			0,15		10,02		29,3	
	SCV 33Bi3839	2,22	0,67	1,81	44,3	0,31	3,10	1,49	0,11	0,03	0,53			0,06		8,40		37,0	
	SCV 3333BF4013	1,14	1,16	4,77	47,1	0,22	2,09	3,54	0,18	0,03	1,02			0,20		12,51		26,1	
	SCV 37af4167	2,73	0,94	2,64	50,2	0,19	1,93	2,87	0,11		0,59					9,00		28,8	
	SCV 37af4179	1,78	1,82	2,76	43,0	0,00	3,70	2,60	0,13		0,76			0,11		11,21		32,2	
	SCV 45M4260	3,06	0,51	2,30	42,9	0,55	2,41	2,56	0,17		0,67					7,88		37,1	
Blue	SCV 4i365	2,78	0,80	2,35	42,0	0,47	3,10	3,39	0,16	0,02	1,97	0,39	0,15	0,11		9,96		32,4	
	SCV 10ef175	2,40	0,64	2,47	40,1	0,58	2,87	2,78	0,16		2,36	0,51	0,22	0,38		8,52		36,0	
	SCV 10DF7637	1,96	0,61	2,16	41,3	0,21	1,76	2,22	0,14		1,46	0,46	0,13	0,96		14,27		32,4	
	SCV 14CF2686	2,01	0,78	2,19	39,4	0,23	1,97	2,65	0,15		1,51	0,30	0,21	0,45		12,56		35,6	
	SCV 20i2989	2,64	0,76	2,10	40,5	0,34	2,55	2,53	0,12		1,92	0,53	0,23	0,29		8,51		37,0	
	SCV 21AM3076	1,77	0,65	1,66	39,6	0,20	3,09	2,19	0,12	0,09	1,32	0,27	0,14	0,42		8,80		39,7	
	SCV 27i3426	2,29	0,62	1,57	41,6	0,32	2,27	2,17	0,11	0,02	1,72	0,50	0,21	0,42		6,82		39,3	
	SCV 30F7756	2,94	0,50	2,13	47,5	0,16	2,50	2,07	0,13	0,04	1,34	0,20		0,34		9,94		30,2	
	SCV 33Bi3839	2,47	0,72	1,88	42,6	0,31	3,46	2,59	0,20		0,87	0,29	0,12	0,29		9,28		34,9	
	SCV 3333BF4013	1,73	0,60	2,87	40,0	0,15	2,22	2,20	0,15		1,68	0,39	0,21	0,41		18,74		28,6	
	SCV 37af4167	2,37	0,82	2,49	43,4	0,22	1,82	3,02	0,17		1,93	0,50	0,17	0,33		12,09		30,6	
	SCV 37af4179	2,01	0,64	1,85	44,6	0,31	4,15	2,22	0,14		1,85	0,55	0,17	0,27		9,59		31,7	
	SCV 45m4260	3,39	0,39	1,83	41,9	1,00	2,12	1,67	0,12		1,71	0,44	0,23	0,27		8,15		36,8	
	SCV 86i4886	2,53	0,72	2,22	43,2	0,35	3,73	3,15	0,12	0,02	2,09	0,42	0,11	0,05		11,27	0,32	29,7	
Green	SCV 10ef175	1,62	0,87	3,09	39,7	0,36	2,12	4,15	0,20		1,01			2,06		1,46		43,3	
	SCV 21AM3076	1,03	0,91	2,62	37,6	0,33	1,85	3,62	0,19	0,03	0,79			3,29		1,27		46,5	
	SCV 27i3426	1,04	0,74	1,66	34,7	0,39	1,55	2,61	0,11	0,19	0,78			2,71		1,92		51,6	
	SCV 30F7756	1,63	0,95	3,40	42,8	0,27	2,64	3,13	0,21		1,37			3,16		1,76		38,7	
	SCV 37af4167	1,07	1,80	4,75	44,3	0,20	1,73	5,03	0,24	0,05	1,18			2,13		1,83		35,7	
	SCV 37af4179	1,33	0,66	2,44	44,7	0,31	3,82	2,80	0,16		0,69			1,64		1,03		40,4	

		Na_2O	MgO	Al_2O_3	SiO_2	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	NiO	CuO	As_2O_5	SnO_2	BaO	PbO	Bi_2O_3
Amber	SCV 4i365	2,07	0,95	3,49	36,9	0,35	2,71	4,74	0,19		4,75			0,11		1,22		42,5	
	SCV 10DF7637	1,27	0,76	3,76	35,2	0,32	1,98	3,96	0,28		4,51	0,07		0,35		0,42		47,2	
	SCV 20i2989	1,28	0,72	2,25	34,9	0,00	2,42	3,10	0,11		4,67			0,00		1,14		49,4	
	SCV 21AM3076	0,78	0,76	2,38	35,6	0,32	2,26	3,61	0,21	0,02	4,09			0,12		0,53		49,4	
	SCV 27i3426	1,10	0,54	2,06	34,3	0,31	2,01	3,00	0,19		4,89			0,07		0,65		50,8	
	SCV 33Bi3839	0,00	1,05	3,01	35,8	0,40	3,09	4,31	0,19		5,22			0,06		0,00		46,9	
	SCV 3333BF4013	1,92	0,90	4,92	44,8	0,19	3,28	4,13	0,29	0,05	4,75			0,00		1,16		33,6	
	SCV 45m4260	2,32	0,60	2,34	42,7	0,37	3,25	2,62	0,18	0,05	2,47			0,11		8,03		35,0	
Brown	SCV 4i365	1,06	1,20	3,26	33,8		2,68	5,30	0,19	2,92	3,51					1,07	0,29	44,8	
	SCV 10DF7637	1,49	0,59	3,12	42,5		2,16	2,29	0,20	3,07	1,53			0,15		0,00	0,26	42,6	
	SCV 30F7756	1,95	0,85	3,19	44,1	0,16	4,80	3,12	0,23	2,67	2,68			0,28		1,50	0,00	34,5	
	SCV 33Bi3839	1,65	0,84	3,10	40,4	0,31	3,46	3,91	0,20	2,94	1,68			0,09		1,54	0,19	39,7	
	SCV 3333BF4013	1,43	1,21	5,36	46,5	0,19	2,78	4,47	0,24	2,60	2,44			0,00		1,12	0,32	31,3	
	SCV 37af4167	0,83	1,04	3,19	41,3	0,20	1,53	3,52	0,15	1,47	1,51			1,36		0,93	0,00	43,0	
	SCV 37af4179	1,52	0,68	2,47	42,3	0,32	4,13	2,86	0,17	3,28	1,38			0,15		0,78	0,18	39,8	
	SCV 45M4260	1,67	0,63	2,55	38,2	0,30	2,45	2,86	0,17	4,85	1,87			0,07		0,97	0,35	43,0	
White	PNS 07	2,97	0,44	1,95	39,9	0,63	3,63	1,95	0,20		0,46					7,58		40,3	
	PNS 08	1,78	0,48	1,73	38,4	0,69	3,22	2,30	0,11		0,51			0,17		7,64		43,0	
	PNS 09	2,60	0,29	1,35	35,6	0,99	2,08	1,17	0,00	0,15	0,25			0,20		7,90		47,4	
	PNS 10	1,79	0,32	1,47	37,3	1,30	2,62	1,21	0,08		0,28			0,20		7,32		46,1	
	PNS 11	1,89	0,31	0,89	35,4	0,88	2,91	1,19	0,06		0,25			0,13		8,27		47,9	
	PNS 12	2,48	0,45	2,64	42,7	0,75	3,23	1,84	0,10		0,51					5,07		40,3	
	PNS 18	2,62	0,72	2,38	39,9	0,96	3,15	2,78	0,12		0,49			0,11		7,89		38,9	
	PNS 20	1,93	0,36	1,65	37,6	0,82	1,43	1,77	0,12		0,40		0,22			6,03		47,8	
	PNS 21	2,13	0,61	2,28	41,1	0,51	1,49	2,89	0,15		0,61		7,80			0,00		40,5	
	PNS 22	2,47	0,45	3,19	41,6	0,34	1,39	2,62	0,17	0,05	0,85					4,73		42,2	
	PNS 23	2,73	0,44	1,70	42,1	0,82	3,77	1,87	0,12		0,39					6,64		39,4	
	PNS 24	2,65	0,90	1,52	47,1	1,03	1,86	1,68	0,10		0,43					7,15		35,6	
	PNS 25	2,63	0,57	2,68	46,3	0,75	3,14	3,10	0,16		0,71					6,71		33,2	
	PNS 26	2,59	0,64	3,23	43,4	0,60	3,57	3,60	0,16		0,68					5,60		36,0	
	PNS 27	2,48	0,65	1,56	40,0	0,99	1,82	1,32	0,13		0,36			0,09		8,64		42,0	
	PNS 28	1,73	0,64	2,34	43,5	0,57	3,74	2,53	0,16		0,78			0,16		6,52		37,4	
	PNS 29	2,84	0,46	2,54	44,4	1,00	1,99	1,92	0,14		0,48					5,60		38,7	

		Na_2O	MgO	Al_2O_3	SiO_2	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	NiO	CuO	As_2O_5	SnO_2	BaO	PbO	Bi_2O_3
Blue	PNS 01	3,16	0,41	1,61	35,6	0,58	2,20	1,73	0,11	0,09	1,77	0,43	0,19	0,24		7,67		44,2	
	PNS 07	2,31	0,46	1,84	38,2	0,43	3,86	2,39	0,17	0,18	1,64	0,35	0,19	0,45		7,41		40,1	
	PNS 09	2,52	0,52	2,01	37,9	0,44	2,82	2,69	0,12	0,05	1,93	0,38	0,15	0,25		8,26		39,9	
	PNS 11	2,60	0,31	1,46	38,6	1,30	3,46	1,60	0,09	0,05	1,10	0,30	0,12	0,18		6,85		42,0	
	PNS 20	2,16	0,45	1,85	40,2	0,65	1,66	2,37	0,13		1,76	0,38	0,17	0,43	2,77	6,27		38,8	
	PNS 21	2,52	0,65	2,16	40,8	0,42	1,98	3,12	0,15		2,20	0,51	0,24	0,19		7,56		37,6	
	PNS 22	2,05	0,81	1,75	39,0	0,83	1,04	1,79	0,09		0,80	0,38	0,00	0,00	3,01	7,23		41,3	
	PNS 23	2,46	0,51	2,35	45,1	0,61	4,46	2,61	0,14		1,51	0,42	0,15			6,81		32,9	
	PNS 24	2,12	0,49	2,07	47,6	0,68	2,61	2,04	0,12		1,56	0,30	0,15	0,11		5,67		34,5	
	PNS 25	2,74	0,88	2,85	47,1	0,44	2,87	3,16	0,13		1,10	0,41				5,78		32,5	
	PNS 26	2,16	0,78	2,22	41,7	0,34	2,40	3,65	0,14		0,96	0,22				4,76		40,6	
	PNS 27	2,64	0,63	1,62	41,4	0,95	1,90	1,81	0,11	0,04	1,43	0,45	0,30	0,29		5,59		40,9	
	PNS 28	1,86	0,54	2,34	44,7	0,39	3,91	2,52	0,16	0,04	1,55	0,37	0,15	0,22		7,10		34,2	
	PNS 29	2,94	0,71	2,99	48,0	0,57	1,93	2,45	0,13	0,00	0,92	0,19	0,09	0,00	2,31	4,52		30,7	1,54
Green	PNS 07	1,15	0,61	2,52	40,0	0,24	3,08	3,42	0,23		0,84			2,85		0,78		44,3	
	PNS 09	2,31	0,48	1,98	37,3	0,47	2,54	2,49	0,10		0,84			2,37		6,16		42,9	
	PNS 10	0,80	0,39	2,10	33,8		1,31	2,68	0,11		0,88			2,08		0,70		55,1	
	PNS 11	1,39	0,29	1,72	39,2	0,30	2,88	1,82	0,13		0,63			1,66		2,26		47,7	
	PNS 12	1,30	0,29	2,38	38,0	0,33	1,18	1,80	0,17	0,05	0,77			2,05		1,68		49,8	
	PNS 21	1,03	0,48	2,59	37,8	0,16	1,21	2,89	0,19		0,88			1,51				51,5	
	PNS 22	0,49	0,38	2,34	34,5	0,20	0,81	2,22	0,15		0,75			1,59		0,45		56,4	
	PNS 24	1,29	0,34	1,79	38,1	0,39	1,43	1,98	0,13	0,05	1,05			2,34		2,41		48,7	
	PNS 26	1,09	0,50	2,66	38,3	0,23	2,15	3,36	0,17	0,12	0,96			1,67		1,02		48,0	
	PNS 28	1,53	0,39	2,95	44,4	0,31	3,21	1,72	0,22		1,00			2,17		1,45		40,7	
	PNS 29	0,60	0,50	2,09	39,0	0,22	1,41	2,57	0,12		0,74			2,07		0,45		50,3	

		Na_2O	MgO	Al_2O_3	SiO_2	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	NiO	CuO	As_2O_5	SnO_2	BaO	PbO	Bi_2O_3
Amber	PNS 11	0,63	0,12	1,36	35,4		2,14	0,71			3,92					0,55		55,1	
	PNS 21	0,79	0,55	2,64	37,3	0,14	1,39	3,44	0,17		3,73					0,52		49,4	
	PNS 22	0,50	0,54	2,48	34,2	0,18	1,26	2,68	0,17	0,50	3,77			0,13		0,49		53,2	
	PNS 24	0,84	0,34	2,30	33,5	0,26	1,61	2,08	0,16		4,30			0,14		0,46		54,0	
	PNS 25	0,89	0,88	2,85	41,0	0,24	2,01	4,16			2,91					0,57		44,5	
	PNS 27	0,71	0,31	1,99	40,3	0,25	3,11	1,41	0,13	0,07	3,87					0,69		47,1	
	PNS 29	0,86	0,58	2,54	40,8	0,20	1,88	3,07	0,16		3,31					0,41		46,2	
Brown	PNS 07	1,95	0,75	3,13	40,8	0,00	4,73	4,11	0,11	2,26	1,10			0,25		1,78	0,29	38,7	
	PNS 08	1,88	0,48	1,85	38,1		2,64	2,29	0,15	1,66	0,88			0,24		8,18		41,6	
	PNS 09	2,26	0,54	2,09	37,9	0,40	3,11	2,49	0,11	1,46	0,78			0,24		7,87	0,15	40,6	
	PNS 10	1,93	0,46	1,86	36,8	0,72	2,22	1,52		1,81	0,68			0,37		9,22		42,4	
	PNS 11	0,76	0,24	1,86	33,6		1,97	1,55	0,11	5,28	0,74			0,23		0,45	0,12	53,1	
	PNS 18	2,04	0,68	2,80	41,2	0,49	4,02	2,82	0,17	1,61	1,15			0,15		5,98		36,9	
	PNS 23	1,42	0,38	1,95	40,4	0,29	2,90	1,68	0,16	3,26	1,19					0,48	0,18	45,7	
	PNS 24	0,66	0,52	2,83	40,6	0,24	2,10	2,62	0,20	2,50	1,78					0,53		45,4	
	PNS 25	1,38	0,67	2,85	40,2	0,32	1,80	3,79	0,20	1,90	0,87					0,81		45,3	
	PNS 27	0,85	0,26	1,88	39,3	0,25	2,65	1,40	0,16	2,56	0,93			0,11		0,52	0,14	49,0	
	PNS 28	1,34	0,41	2,05	38,6	0,29	2,68	1,69	0,16	3,37	1,37						0,19	47,9	
	PNS 29	0,95	0,94	2,70	40,9	0,19	1,86	3,96	0,18	2,37	0,82					0,63		44,5	

blue and white samples form a distinct group, but a large number of the SCV samples are separated from this set because of their high SnO_2 content.

In regard to white glazes, the results obtained for tin oxide contents in the PNS collection are similar to those from previous analyses of Hispano-Moresque ceramics (Chabanne *et al.* 2008; Molera *et al.* 1997; 2001b; Pérez-Arantegui *et al.* 2005; 2009). Higher tin oxide contents, such as the ones identified in the SCV samples, have been identified in Islamic white glazes from Zaragoza and Córdoba (Molera *et al.* 2001b). These high-tin glazes cannot be differentiated from the others by decoration technique or decorative pattern (both *arista* and *cuerda-seca* tiles are found in this group). A larger number of samples will be analysed to assess other possible differences regarding chemical composition or morphology.

Five coloured glazes were identified in the two collections under study: white, blue, green, brown and amber. White and blue glazes, as already mentioned, are opacified with tin oxide (*c.* 5–14 wt% SnO_2). Colours are obtained by adding metallic oxides to the glaze: cobalt oxide (CoO) for blue, copper oxide (CuO) for green, manganese oxide (MnO) for brown and iron oxide (Fe_2O_3) for amber. Brown, green and amber show much lower SnO_2 contents (between *c.* 0–2 wt%). Exceptionally, in relief tiles from the PNS, brown and green seem to have been painted over (or under) a white tin-glaze base, thus presenting higher tin oxide contents.

The analysis of blue glazes revealed the same iron-cobalt-nickel-copper (Fe-Co-Ni-Cu) association in the large majority of samples, with manganese (Mn) also detected in most of them. In the PNS collection, however, the presence of arsenic (As) was identified in samples PNS20, PNS22 and PNS29.

These differences do not necessarily mean that cobalt was imported from more than one location. All of the above mentioned cobalt associations existed in the mining district of Erzgebirge (Saxony), in Germany, which was the most important cobalt source at that time (Zucchiati *et al.* 2006; Roldan *et al.* 2006). The Fe-Co-Ni-Cu association has also been identified in Italian and Spanish ceramics from the 14th-16th centuries, where copper is present mostly up until the 16th century and nickel is only evident from the 15th century onwards (Roldan *et al.* 2006). The presence of arsenic (As) in the blue pigment composition has been associated with a change in the production of zaffre (calcinated cobalt ore, mixed with sand) which occurred *c.* 1520 in the Saxony region (Zucchiati *et al.* 2006). Thus, arsenic-containing samples could have been manufactured after 1520.

Glaze technology

The glazes in both collections are mostly homogeneous, with few mineral inclusions and gas bubbles. Bubbles are usually formed by organic matter that burns during the firing of the tile. They can travel up to the surface of glaze or, if the glaze is too viscous, they remain trapped inside it. The scarcity of gas bubbles in these glazes suggest the use of frits, and/or high firing temperatures and long firing and cooling times (Pradell *et al.* 2010).

The homogeneity that is observed in most glazes is coherent with the use of frits. Studies of Islamic and Hispano-Moresque ceramics from several archaeological excavations have revealed that a simplification occurred over the centuries, where the fritting process was progressively abandoned in Hispano-Moresque workshops. This was observed for transparent lead glazes, and it was probably a means of making the process less expensive. In tin-opacified glazes, changes in the fritting process also occurred, as earlier Islamic glazes are usually more homogenous and exhibit smaller and more homogenously distributed tin oxide particles than Hispano-Moresque ones (Molera *et al.* 1997; 2001b; Vendrell-Saz *et al.* 2006).

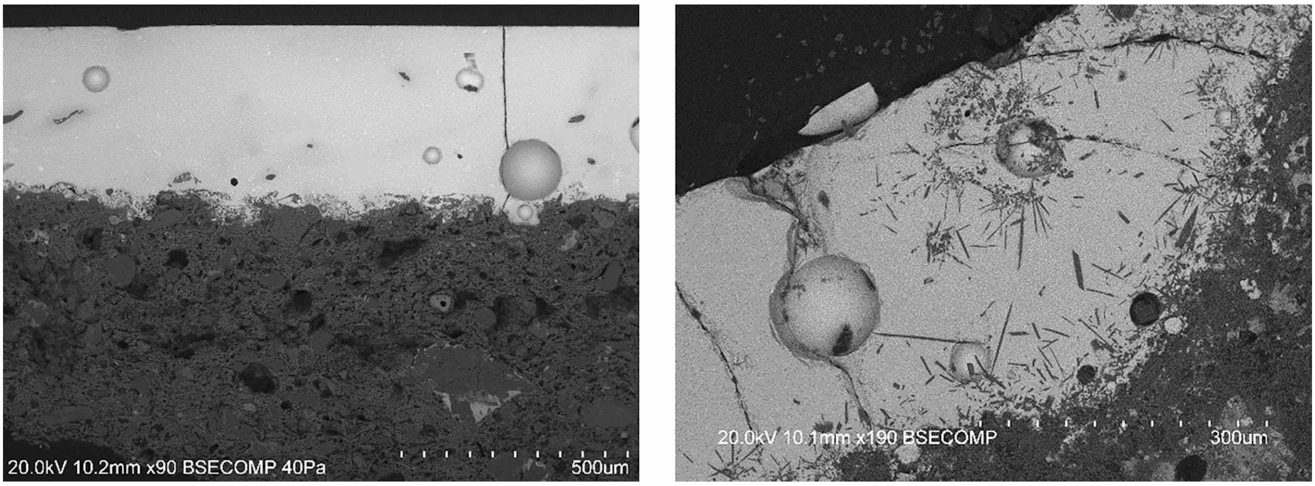


Figure 3. BSE image of a typical glaze-ceramic interface found in white glazes (3A – PNS 12) and in brown glazes (3B – SCV 33Bi3839). (Image: Authors).

The glaze-ceramic interface

The glaze-ceramic interface is a valuable source of information regarding the production technique: its thickness and mineralogical composition strongly depend on firing temperature and duration, and on the chemical composition of both the ceramic body and the glaze (Molera *et al.* 2001a).

Figure 3A illustrates the typical glaze and glaze-ceramic interface found in white and blue glazes, and Figure 3B in amber glazes. Thicker interfaces (up to 100 μm) are visible in brown and amber glazes in the SCV collection, whereas in the PNS samples the highest thickness was measured as *c.* 70 μm. Although these values suggest a single-fire process (Molera *et al.* 2001a), specific experiments for tin-glazed ceramics are being performed in order to clarify this hypothesis.

Chemical analysis of the mineral inclusions in the interface (through EDS and μ-Raman) revealed differences between the PNS and SCV collections. Through μ-Raman analysis, mostly potassium feldspars were identified in the glaze-ceramic interface of the PNS samples (orthoclase and microcline, $KAlSi_3O_8$). In the SCV samples, calcium-rich minerals are more frequent, such as wollastonite ($CaSiO_3$). Magnesium-rich crystals (diopside $MgCaSi_2O_6$) and quartz (SiO_2) were observed in both collections. Fig. 4 illustrates the main difference between most SCV and PNS samples, where a calcium-rich layer can be seen in the first ones, but a potassium-rich interface prevails in the latter.

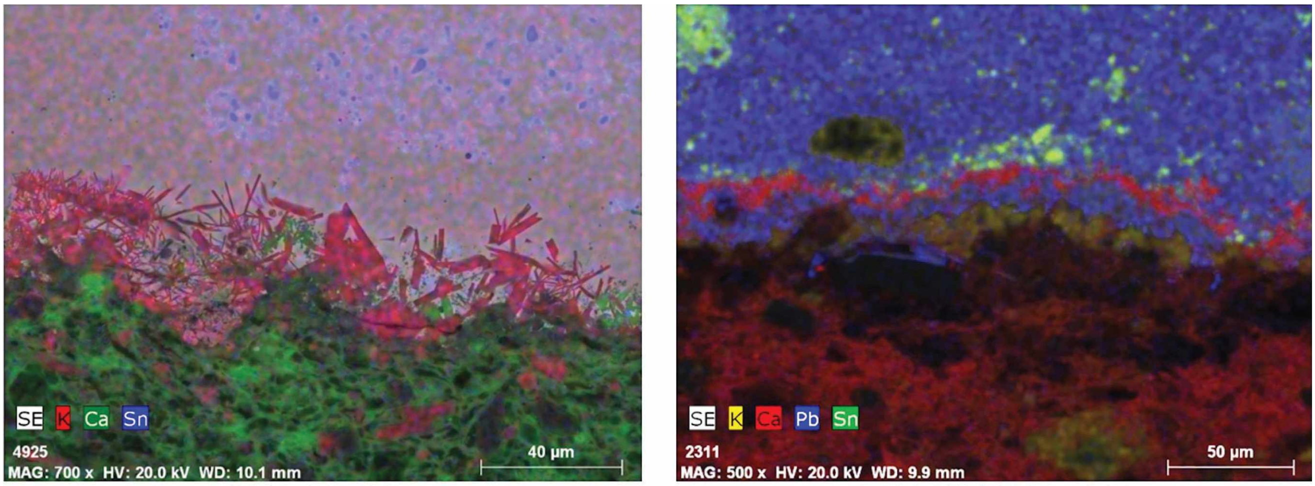
Ceramic body

The ceramic body of Hispano-Moresque tiles is generally thick, measuring between 19 and 22 mm. In relief tiles from the PNS collection, the thickness is as high as 26 mm. Both Portuguese collections exhibit similar visual characteristics: creamy buff coloured fabrics, sometimes with a pinkish hue, define the majority of the samples, with mineral inclusions being perceptible to the naked eye.

The ceramic bodies of all of the analysed samples are calcareous (*c.* 14–25 wt% CaO), which corresponds with their colour, which ranges from a light creamy tone to a more pinkish hue. Calcareous clays were preferred for tin-glazed ceramics for two reasons: firstly they provide a light-coloured ground for the glaze, reducing the amount of tin necessary to achieve a white colour (tin was a relatively expensive material), and, secondly, the thermal expansion is compatible with the glaze, reducing production-related defects (Molera *et al.* 1998; Tite 2008).

The creamy hue relates both to the calcium-rich nature of the clays and the firing temperature and duration. A firing temperature of *c.* 900–950°C is necessary to achieve a complete decomposition of calcite and the formation of pyroxenes and other phases that will incorporate iron ions in their structure. Thus, less iron oxides will form that would otherwise contribute to reddish hues (Molera *et al.* 1998). However, calcite has been identified in most samples and it can also be a result of a post-depositional re-carbonation process. This is a very common process and occurs mainly on the surface of the sample (Fabbri *et al.* 2014; Molera *et al.* 1998).

Table 3 shows the results for the quantitative analysis performed by μ-PIXE on the ceramic body of both Portuguese collections. The creamy-pink colour of the ceramic body is characteristic for tin-glazed ceramics and corresponds with a calcium-rich composition (*c.* 14–25 wt% CaO), as identified by μ-PIXE analysis. Quantitative analysis through μ-PIXE revealed both collections to have similar compositions. The main constituent oxides are silicon dioxide (SiO_2), calcium oxide (CaO), aluminium oxide (Al_2O_3), iron (III) oxide (Fe_2O_3), magnesium oxide (MgO) and potassium oxide (K_2O), with silicon



PNS 09 white

SCV 45M4260 white

Figure 4. X-ray map of a typical glaze-ceramic interface, with a K-rich layer in PNS collection (4a – PNS 09) and with a Ca-rich layer in SCV collection (4b – SCV 45M4260). (Image: Authors).

Table 3. Chemical composition of the ceramic body, in wt.% average, obtained by µ-PIXE.

	Technique	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CuO	ZnO	PbO
PNS 01	Flat	1,11	3,56	12,2	52,7		0,21	0,04	2,09	23,1	0,45	0,05	3,86			0,16
PNS 07	Relief	1,00	3,82	11,2	51,2		0,30	0,03	1,36	25,5	0,76	0,07	4,32			0,53
PNS 08	Relief	1,14	3,56	12,1	52,5		0,26	0,06	2,03	23,8	0,42	0,06	3,69			0,31
PNS 09	Relief	1,14	4,67	12,2	56,3		0,29	0,19	2,27	18,2	0,46	0,06	4,09			0,10
PNS 10	Relief	1,23	4,03	13,5	53,3		0,30	0,07	2,09	19,3	1,05	0,08	4,38			0,35
PNS 11	*Cuerda-seca*	1,02	3,52	12,8	57,0		0,38	0,14	2,26	17,7	0,53	0,05	4,41			0,19
PNS 12	*Cuerda-seca*	0,86	3,09	11,7	54,7	1,20	0,10	0,02	1,95	21,6	0,50	0,06	4,23			0,06
PNS 18	Relief	1,14	3,78	12,4	56,3		0,16	0,06	1,63	19,3	0,52	0,08	4,12			0,56
PNS 20	*Cuerda-seca*	1,66	4,86	13,0	47,3	0,59	0,30	0,22	1,83	24,1	0,56	0,07	5,12			0,08
PNS 21	*Arista*	1,32	3,81	12,4	52,0		0,25	0,08	1,73	23,7	0,51	0,08	4,02			0,10
PNS 22	*Arista*	0,92	3,48	12,4	56,9		0,36	0,30	1,88	18,3	0,64	0,09	4,77			
PNS 23	*Cuerda-seca*	1,12	4,24	14,5	49,0		0,20	0,11	2,04	22,1	0,64	0,10	5,25	0,19		0,23
PNS 24	*Arista*	1,14	5,77	13,7	48,3		0,26	0,23	2,29	22,0	0,63	0,06	5,15	0,23		0,14
PNS 25	*Arista*	1,10	3,72	12,7	55,9	0,22	0,14	0,16	1,89	18,6	0,59	0,08	4,64			0,20
PNS 26	*Arista*	1,62	4,25	12,5	49,8		0,24	0,76	2,13	22,5	0,75	0,10	5,14	0,22		
PNS 27	*Cuerda-seca*	1,09	4,02	13,2	49,3		0,29	0,53	3,26	22,1	0,66	0,07	4,94	0,26	0,11	0,10
PNS 28	*Cuerda-seca*	1,03	4,85	12,5	51,4		0,29	0,18	1,77	22,1	0,55	0,08	4,90	0,21		0,07
PNS 29	*Arista*	1,25	4,60	12,8	55,5		0,20	0,16	1,96	17,2	0,58	0,06	4,98			0,62
SCV 4i365	*Arista*	1,19	4,89	12,5	51,1		0,20	0,04	1,44	19,4	0,09	4,14	4,51			
SCV 10DF7637	*Arista*	1,04	4,70	12,7	55,1	0,38	0,23	0,06	1,30	18,3	0,68	0,08	5,11			0,23
SCV 10EF175	*Arista*	0,85	4,83	11,8	53,8		0,51	0,07	1,43	17,4	0,13	4,32	4,35			
SCV 14CF2686	*Relief*	1,08	3,81	11,8	53,1	0,21	0,25	0,09	1,55	23,2	0,67	0,08	4,07			0,09
SCV 20i2989	*Arista*	0,89	4,52	13,4	59,4	0,84	0,16	0,07	1,45	12,0	0,85	0,10	6,03			0,18
SCV 21AM3076	*Arista*	1,19	5,64	12,4	50,9		0,22	0,10	1,20	18,9	0,10	4,20	4,45			
SCV 27i3426	*Cuerda-seca*	0,87	7,27	12,1	51,0	0,11	0,18	0,08	2,04	21,8	0,44	0,06	3,93			0,06
SCV 30F7756	*Cuerda-seca*	1,14	4,57	14,4	54,6		0,24	0,09	1,68	17,3	0,63	0,08	5,12			0,16
SCV 33Bi3839	*Cuerda-seca*	1,17	4,24	13,2	53,9		0,21	0,08	1,98	19,3	0,60	0,09	4,82			0,15
SCV 37AF4179	*Arista*	0,81	4,97	13,9	54,9	0,26	0,29	0,12	1,58	16,6	0,76	0,08	5,29			0,37
SCV 45M4260	*Cuerda-seca*	0,82	4,54	14,5	57,4	0,80	0,21	0,04	1,68	13,5	0,78	0,09	5,53		0,17	
SCV 86i4886	Flat	1,12	5,70	12,2	53,2		0,30	0,05	1,49	20,6	0,51	0,09	4,76			
SCV SPF8435	*Arista*	0,48	4,58	14,5	59,8			0,07	1,69	14,3	0,80		2,84			0,94
SCV SPM8434	*Arista*	0,49	4,62	17,1	56,0	0,07	0,02	0,06	2,69	14,8	0,71	0,04	2,81			0,54

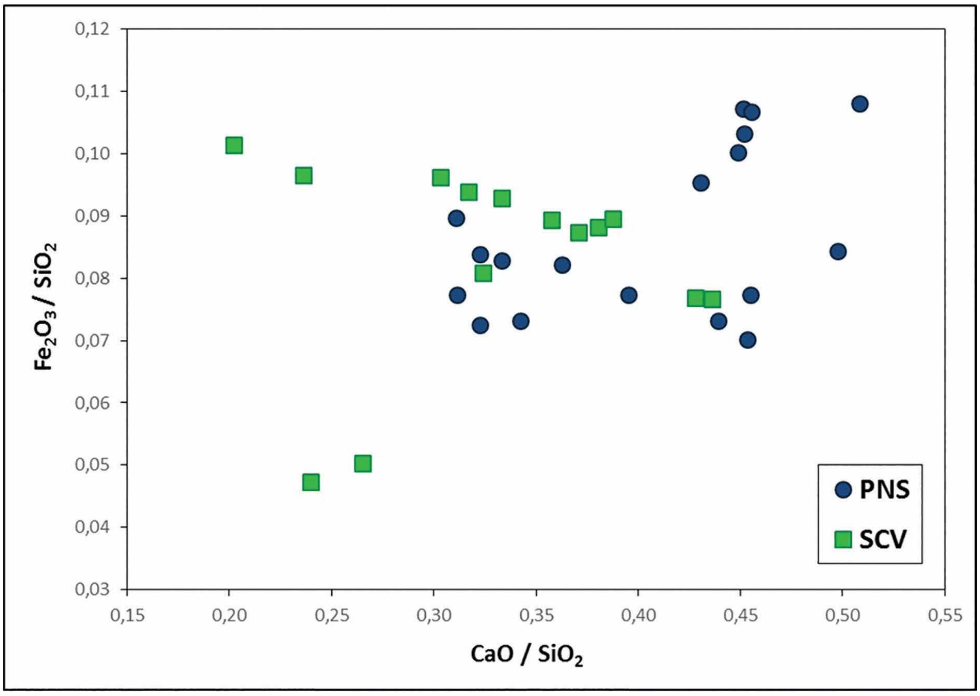


Figure 5. Fe_2O_3/SiO_2 vs. CaO/SiO_2 ratios of the ceramic body of analysed samples from the two collections (results obtained by µ-PIXE). (Image: Authors).

dioxide (SiO_2) values ranging between 47–57 wt% (PNS) and 51–60 wt% (SCV), and calcium oxide contents between 18–25 wt% (PNS) and 12–23 wt% (SCV).

In Fig. 5, differences can be observed between the collections. The SCV samples show a group with an inverse relationship between iron (III) oxide (Fe_2O_3) and calcium oxide (CaO) contents. On the other hand, the PNS collection shows greater variability in results, with a sub-set being characterised by a higher iron (III) oxide (Fe_2O_3) and calcium oxide (CaO) contents.

The two samples with lower iron (III) oxide / silicon dioxide (Fe_2O_3/SiO_2) ratios are unglazed *arista* tiles from the SCV collection. These two samples have a lighter yellowish colour and are thinner than the other *arista* tiles from the collection. They also exhibit a more perfect technique, although the decorative patterns are both very common in Coimbra and in other Hispano-Moresque tile collections both in Portugal and Spain. Thus, these specific tiles could have been produced in a later period, probably to replace others in the Monastery that were damaged during the floods or to decorate the new monastery of Santa Clara-a-Nova.

Conclusions

Hispano-Moresque tiles combine the technology of both tin-opacified and transparent lead glazes. These are all lead-rich glazes, with lead oxide (PbO) contents of 26–48 wt% for tin-opacified glazes (mostly blue and white) and 34–56 wt% for transparent lead glazes (mostly green, amber and brown). Exceptionally, in relief tiles from the Palácio Nacional de Sintra, brown and green seem to have been painted over (or under) a white tin-glaze ground, thus presenting higher tin oxide contents than the other brown and green glazes in this study.

The tin oxide content is the main difference between the two collections. Amongst the PNS samples the tin oxide value does not exceed 9 wt%, corresponding with the literature on Hispano-Moresque tin-glazed ceramics. However, approximately half of the SCV samples had a tin oxide (SnO_2) content above 10 wt%, suggestive of Islamic technology.

The ceramic body of all samples is calcareous (12–25 wt% calcium oxide), as expected for tin-glazed Hispano-Moresque ceramics. Two SCV samples show lower iron oxide contents and exhibit a different lighter colour than the rest of the set. They correspond to unglazed *arista* tiles and are probably later in date.

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Résumé

Cet article examine les carreaux vernis hispano-mauresques (15ème -16ème siècles) qui provenaient des collections du Palácio Nacional de Sintra et Mosteiro de Santa Clara-a-Velha, au Portugal. Un nombre représentatif de carreaux des deux collections a été analysé par μ-PIXE, SEM-EDS et spectrométrie Raman μ, afin de caractériser morphologiquement et chimiquement chaque collection. Cette étude est incluse dans un projet plus large qui concerne la caractérisation de carreaux médiévaux espagnols et portugais et leur provenance.

Zusammenfassung

Dieser Beitrag untersucht spanisch-maureske Kacheln (15.-16. Jahrhundert) aus den Sammlungen des Palácio Nacional de Sintra und des Mosteiro de Santa Clara-a-Velha in Portugal. Eine repräsentative Anzahl an Kacheln aus den beiden Sammlungen wurde anhand von μ-PIXE (Partikel-induzierte Röntgenemission), SEM-EDS (Rasterelektronenmikroskopie mit Röntgen-Mikroanalyse) und μ-Raman-Spektrometrie ausgewertet. So werden die beiden Sammlungen sowohl chemisch als auch morphologisch beschrieben. Die vorliegende Studie ist Teil eines größeren Projektes, das sich mit der Charakterisierung und Provenienz portugiesischer und spanischer Kacheln aus dem Mittelalter befasst.