

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

XRF Characterization Of 18th Century Piedmontese Porcelains From The Palazzo Madama Museum (Torino, Italy)

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1631682> since 2017-04-19T10:35:14Z

Published version:

DOI:10.1111/arcm.12186

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)



UNIVERSITÀ DEGLI STUDI DI TORINO

*This is an author version of the contribution published on:
Questa è la versione dell'autore dell'opera:*

XRF CHARACTERIZATION OF XVIII CENTURY PIEDMONTESE
PORCELAINS FROM THE PALAZZO MADAMA MUSEUM (TORINO, ITALY)

Archaeometry, Volume 58, Issue 5

October 2016

Pages 765–778

DOI: 10.1111/arcm.12186

*The definitive version is available at:
La versione definitiva è disponibile alla URL:*

<http://onlinelibrary.wiley.com/doi/10.1111/arcm.12186/full>

XRF CHARACTERIZATION OF XVIII CENTURY PIEDMONTESE PORCELAINS FROM THE PALAZZO MADAMA MUSEUM (TORINO, ITALY)

F. TURCO^{1,*}, P. DAVIT^{1,2}, C. MARITANO³, L. OPERTI^{1,2}, G. FENOGLIO¹, A. AGOSTINO^{1,2}

¹Università di Torino, Dipartimento di Chimica, Via Pietro Giuria 7, 10125 Torino, Italy.

²NIS Center, Università di Torino, Via Gioacchino Quarello 15A, I-10135 Torino, Italy.

³Fondazione Torino Musei, Palazzo Madama Museo Civico d'Arte Antica, Piazza Castello, Torino, Italy.

*Corresponding author.

ABSTRACT

Around 100 porcelain objects of the XVIII century Rossetti, Vische and Vinovo manufactures (Piedmont, Italy) from the Palazzo Madama Museum collection were analyzed by means of a X-Ray Fluorescence portable detector. The present study represents the first chemical characterization of these early (1737-1825) European porcelains. Chemical composition data were submitted to multivariate clustering techniques that underlined a complete classification of the three manufactures and the presence of three subgroups for Vinovo production. These resulting subgroups did not mirror the classification expected on the basis of the historiographical literature. The overall data pointed to a technological continuity not only through all the Vinovo phases but even from the earlier Vische manufacture.

Keywords: Porcelains, Vinovo, Vische, Rossetti, Piedmont (Italy), XVIII Century, portable XRF analysis

INTRODUCTION

In the XVIII Century three porcelain manufactures (Rossetti, Vische and Vinovo, see Figure 1) were planted in Turin (Piedmont, Italy) or its neighbourhood (Brosio 1973). Rossetti manufacture was a well renowned *maiolica* manufacture since the delivery of *Regie Patenti* (royal licenses) in 1725. In 1737 the licenses were extended to the production of porcelain and in 1742 the secrets of porcelain production reached Turin (from Du Paquier manufacture) by way of Jakob Helchis. Nevertheless,

unavailability of kaolin did not allow to exceed the experimental phase and very few pieces of porcelain were produced. Three of these pieces were historically identified in the collection of Palazzo Madama Museum. Piedmontese porcelain production resumed in 1765 when Ludovico Birago, Comte of Vische, obtained the *Regie Patenti* and founded a company, after ten years of secret experiments. Vische porcelain production was technically quite successful, notwithstanding various problems pending the firing step (collapsed or scorched pieces) but the company failed and closed in 1768.

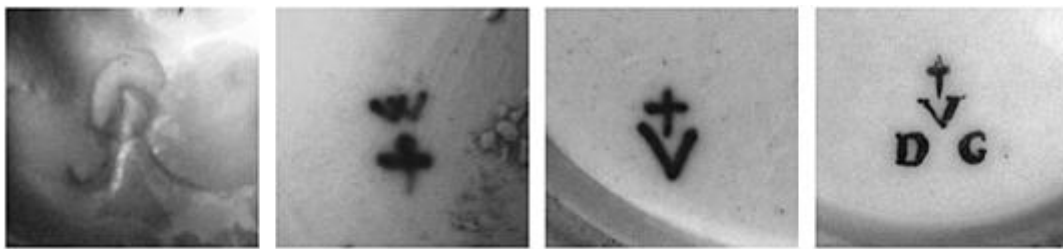


Figure 1: From left to right: marks of Rossetti, Vische and Vinovo manufacture. Last picture shows a specific mark of the Vinovo manufacture pending the Gioanetti conduction ('DG' for Doctor Gioanetti).

All the plant equipments and unsold products were taken over by Giovanni Vittorio Brodel, who planted a new factory in the Vinovo Castle in 1776, with several craftsmen already working at Vische and with the technical support of Pierre Antoine Hannong, an arcanist from Paris. Hannong conduction gained great technical achievement but very little commercial success and in 1780 the factory was sequestered and the stocks went up for auction. Most of the materials (objects both to be decorated and to be sold, waste to be ground and raw materials) were purchased by the doctor and chemist Vittorio Amedeo Gioanetti, who was charged with the conduct of the manufacture of Vinovo, once again with some of the same artists and craftsmen. At last, this new conduct brought international success to Vinovo production, both from the commercial and the technical points of view. In fact the historical literature gives credit to Gioanetti to have overcome the problem of kaolin lack in Italy, employing “*magnesite di Baldissero*” with a little amount of clay (Brosio 1973; Malaguzzi 1987). The high quality of Gioanetti porcelains is testified by their inclusion in the Napoleonic *Enquête* started in 1805 with the aim of collecting recipes from the “*fabriques les plus considérable de poterie*”(Malaguzzi 1987, p.95). Gioanetti recipes were then reported by Brongniart in his *Traité* (Brongniart 1844), Figure 2. In the third and last period Vinovo manufacture was conducted by Giovanni Lomello, after Gioanetti death in 1815. Lomello did not introduce any technological improvement and in few years he brought Vinovo plant to a definitive closure.

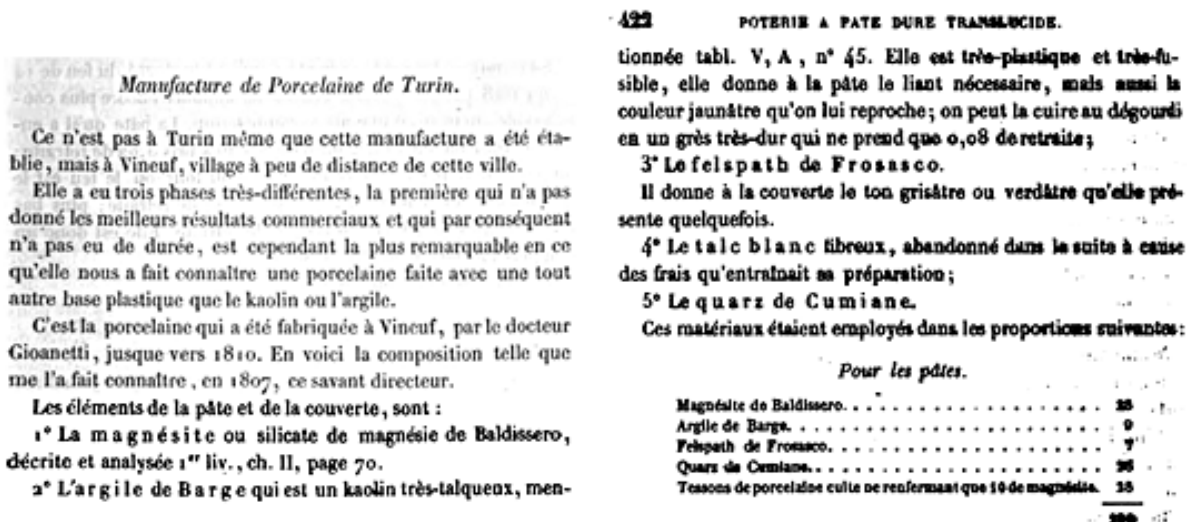


Figure 2: Brongniart, *Traité des arts céramiques ou des poteries* (1844) vol. II, pp. 421-422.

The present paper represents the first archaeometric evaluation on Rossetti, Vische and Vinovo porcelain classes (the only previously published data is reported by Freestone on a Rossetti piece from the British Museum (Freestone et al. 2003)). A chemical characterization of these manufactures was carried out with the final aims of exploring the technology of production, obtaining the chemical profile of each manufacture and solving several questionable attributions. A special focus was dedicated to the Vinovo manufacture in order to distinguish between Hannong and Gioanetti phases. The excellent condition of the collections with the total absence of fractures or fragments leads to the need of employing a not invasive technique, as portable X-Ray Fluorescence (XRF). In fact, XRF is a powerful, fast, and not destructive technique, particularly suitable in the case of *in situ* analyses of numerous and/or precious samples; thanks to these features its application in the artistic/museum context is well known (Casadio & Bezur 2009). In the case of porcelain the choice of the raw materials and the formulation of the recipes were particularly studied in order to determine the final outcome, in terms of macroscopic appearance and technological features. Of course, XRF allows only the determination of which elements are present and in which amount and does not allow to obtain information on the kind of source(s) where a particular element come from (Casadio & Bezur 2009). Nonetheless, the knowledge of the historical recipes and the comparison between manufactures allows to make some speculation on the adopted formulation of pastes and glazes.

MATERIALS AND METHODS

In the present work the following samples were analyzed: 3 Rossetti objects (the overall Rossetti

porcelain *corpus* in the Palazzo Madama collection), 9 pieces from Vische manufacture and 79 objects from Vinovo production selected from the three Hannong, Gioanetti and Lomello periods, together with several pieces of uncertain assignment (see Table 1). The materials showed the most diverse shapes and finishes, ranging from the ornate candle holder produced for the International Exhibition of 1811, figurines and groups of figurines in biscuit, decorative objects or tableware. All the pieces are conserved in *Palazzo Madama, Museo Civico di Arte Antica* of Torino (Italy).

Table 1: List and description of the analyzed objects with the corresponding stylistic and scientific attributions.

Catalogue code	Object	Stylistic attribution	Scientific attribution
1054/c	decorated cup	Rossetti	Rossetti
3190/c1	glazed figurine	Rossetti	Rossetti
3190/c2	glazed figurine	Rossetti	Rossetti
2260/c	decorated jar	Rossetti or Vezzi?	Rossetti
uncatalogued	decorated cup	Vische	Vische
1975/c	glazed figurine	Vische	Vische
1982/c	glazed figurine	Vische	Vische
1998/c	glazed figurine	Vische	Vische
1999/c	glazed figurine	Vische	Vische
2271/c	glazed jar	Vische	Vische
3189/c	glazed figurine	Vische	Vische
3191/c	glazed figurine	Vische	Vische
3192/c	glazed figurine	Vische	Vische
1974/c	figurine, biscuit	Vinovo?	None
787/c	glazed (and gilded) cup	Vinovo G	Vinovo
824/c	decorated coffee cup	Vinovo G	Vinovo
1306/c	glazed figurine	Vinovo	Vinovo
1315/c	glazed (gray) medallion	Vinovo H	Vinovo
2193/c	decorated plate	Vinovo G	Vinovo
2194/c	decorated coffee cup	Vinovo G	Vinovo
2196/c	glazed plate	Vinovo G	Vinovo
3162/c	glazed figurine	Vinovo H?	Vinovo
3188/c	glazed figurine	Vinovo?	Vinovo
3251/c	glazed cup	Vinovo G	Vinovo
861/c	decorated coffee pot	Vinovo G	Vinovo G/L
1314/c	medallion, biscuit	Vinovo L	Vinovo G/L
1943/c	figurine, biscuit	Vinovo G or Capodimonte?	Vinovo G/L
1946/c	figurine, biscuit (1817)	Vinovo L	Vinovo G/L
1952/c	figurine, biscuit	Vinovo L	Vinovo G/L
1960/c	figurine, biscuit	Vinovo G?	Vinovo G/L
1986/c	figurine, biscuit (1817)	Vinovo L	Vinovo G/L
1989/c	pedestal, biscuit (1817)	Vinovo L	Vinovo G/L
1991/c	figurine, biscuit	Vinovo G?	Vinovo G/L

1995/c	figurine, biscuit (1791)	Vinovo G	Vinovo G/L
1997/c	figurine, biscuit	Vinovo L	Vinovo G/L
2001/c	figurine, biscuit (1818)	Vinovo L	Vinovo G/L
2002/c	figurine, biscuit (1792)	Vinovo G	Vinovo G/L
2009/c	medallion, biscuit	Vinovo H?	Vinovo G/L
2016/c	figurine, biscuit (1817)	Vinovo L	Vinovo G/L
2020/c	figurine, biscuit (1816)	Vinovo L	Vinovo G/L
2023/c	figurine, biscuit (1817)	Vinovo L	Vinovo G/L
2143/c	glazed (and gilded) coffee pot	Vinovo G?	Vinovo G/L
2144/c	glazed (and gilded) eyewash	Vinovo G	Vinovo G/L
2162/c	decorated tea box	Vinovo G	Vinovo G/L
3161/c	decorated figurine	Vinovo H?	Vinovo G/L
3196/c	decorated jar	Vinovo G	Vinovo G/L
3207/c	decorated coffee pot	Vinovo G	Vinovo G/L
3227/c	decorated tea pot	Vinovo G	Vinovo G/L
3392/c	figurine, biscuit	Vinovo H or G?	Vinovo G/L
1300/c	glazed figurine	Vinovo H?	Vinovo G/L?
3211/c	decorated plate	Vinovo H	Vinovo G/L?
392/c	decorated tea box	Vinovo H	Vinovo H1
699/c	glazed figurine	Vinovo H or G?	Vinovo H1
842/c	decorated button	Vinovo H	Vinovo H1
1132/c	decorated tea box	Vinovo H	Vinovo H1
1891/c	clock housing, biscuit	Vinovo H?	Vinovo H1
1970/c	glazed figurine	Vinovo H?	Vinovo H1
1973/c	glazed figurine	Vinovo H or G?	Vinovo H1
1983/c	glazed figurine	Vinovo H or G?	Vinovo H1
2003/c	glazed figurine	Vinovo H?	Vinovo H1
2008/c	glazed medallion	Vinovo H	Vinovo H1
2015/c	glazed figurine	Vinovo H?	Vinovo H1
2022/c	" <i>Allegoria dello Stato Sabauda</i> ", biscuit	Vinovo H or G?	Vinovo H1
2142/c	decorated coffee pot	Vinovo H or G?	Vinovo H1
2199/c	decorated candle holders	Vinovo H or G?	Vinovo H1
3145/c	decorated figurine	Vinovo H or G?	Vinovo H1
3148/c	decorated chocolate pot	Vinovo H?	Vinovo H1
3165/c1	glazed figurine	Vinovo	Vinovo H1
3165/c2	glazed figurine	Vinovo H?	Vinovo H1
3168/c	decorated figurine	Vinovo H or G?	Vinovo H1
3170/c	glazed figurine	Vinovo H?	Vinovo H1
3178/c	decorated figurine	Vinovo H or G?	Vinovo H1
3179/c	decorated figurine	Vinovo H or G?	Vinovo H1
3180/c	decorated figurine	Vinovo H or G?	Vinovo H1
3181/c	decorated figurine	Vinovo H or G?	Vinovo H1
3186/c	glazed figurine	Vinovo H?	Vinovo H1
3194/c	" <i>Sant'Uberto</i> ", biscuit (Tamietti)	Vinovo H	Vinovo H1
3195/c	" <i>Allegoria dello Stato Sabauda</i> ", biscuit	Vinovo H	Vinovo H1
3226/c1	decorated vase	Vinovo	Vinovo H1
3233/c	decorated chocolate pot	Vinovo H	Vinovo H1

391/c	decorated coffee pot	Vinovo G	Vinovo H1?
786/c	decorated tea box	Vinovo G	Vinovo H1?
833/c	decorated coffee pot	Vinovo G	Vinovo H1?
1316/c	decorated candle holder	Vinovo G	Vinovo H1?
1987/c	figurine, biscuit (1818)	Vinovo L	Vinovo H1?
2169/c1	glazed small pan	Vinovo G	Vinovo H1?
2169/c2	glazed small pan	Vinovo G	Vinovo H1?
2178/c	decorated candle holder	Vinovo G	Vinovo H1?
2203/c	decorated candle holder	Vinovo G	Vinovo H1?
3164/c	glazed figurine	Vinovo G	Vinovo H1?
1653/c	medallion, biscuit	Vinovo H or G?	Vinovo H2
1883/c	glazed figurine	Vinovo H or G?	Vinovo H2
1884/c	decorated figurine	Vinovo H or G?	Vinovo H2
2012/c	vase, biscuit	Vinovo?	Vinovo H2
3203/c	decorated soup tureen (1778)	Vinovo H	Vinovo H2
2392/c	decorated coffee pot	Vinovo G?	Vinovo H2?
2271/c	decorated jar	Vezzi	-
2495/c	figurine, biscuit	Capodimonte	-

Analyses were performed both on the glaze, when present, and on the paste. As for the paste, analyses were performed (with the obvious exception of the biscuit pieces) on completely unglazed areas of the objects (when suitable), such as base ring in the case of plates or cups or the bottom surfaces of figurines and vases. To completely avoid contamination these unglazed surfaces were gently scraped off with a diamond disk, moved by hand in order to avoid dangerous vibration. Analyses were performed with a EDXRF Thermo NITON (USA) XL3T-900-GOLDD spectrometer, equipped with a silver target and a large area silicon drift detector (SDD) with an energy resolution of 136 eV calculated at 5.9 keV. The used geometry is 30°/30°, with a working distance of 2 mm orthogonal to the detector/source plane. Total analysis time is 120 seconds, subdivided in 4 fractions of 30 seconds each, at different energetic ranges (high: 50keV, 50µA, Mo filter; main: 40keV, 50µA, Fe/Al filter; low: 20keV, 95µA, Cu filter; light: 6keV, 95µA, without filter). Spectra were processed by the WinAxil commercial software (from the IAEA academic software). The instrument was kept in position by a custom stage allowing micrometric movements. All measurements were conducted in air with a small spot (3 mm diameter) since the shape and decoration of the objects make the surface very uneven. In this way it was possible to irradiate exclusively colorless glaze or unglazed areas for the analysis of the glazes and the pastes, respectively. In order to evaluate Mg abundance, analyses in helium were conducted, with a 4 ml/min flow.

In order to validate quantitative analyses, measurements on certified composition standards were conducted. As for the pastes the used Certified/Standard Reference Materials (CRM or SRM) were the SRM 98b (plastic clay) from the National Institute of Standards and Technology (NIST),

Gaithersburg, MD, USA and the CRM SARM69 (powdered ceramic) from MINTEK, Johannesburg, SA. Powdered standard were pressed with a 12 tons hydraulic press to obtain 1 cm diameter and 2 mm thickness pellets. For the glazes the CRM SGT4, SGT7, SGT8 and SGT10 from the “Society of Glass Technology”, Sheffield, UK and the CRM 612 from the NIST were used.

Element concentrations were obtained applying a correlation coefficients approach, by using the De Jong algorithm (Rousseau 2001) and, in some cases, a Fundamental Parameter (FP) approach by means of a partial least square method (Van Espen 2000). The use of a mixed approach in the XRF data analysis is due to the influence of heavy (lead, in the present case) on light elements when they are simultaneously quantified. Moreover the presence of a not quantifiable amount of voids in the analysed volume introduces (especially in the body analysis) an elevated uncertainty. To take into account these potential sources of errors, the fundamental parameter approach was followed by a correction based on correlation coefficients (obtained analyzing reference materials and ad hoc synthesized samples).

Statistical evaluations were performed on the results obtained for 9 elements (Sn, Rb, Pb, Fe, Ti, Ca, K, Al and Si) using the open access R software (R Core Team (2013)) and the software XLSTAT, Addinsoft. Two unsupervised methods were used to show the XRF data in a multi-dimensional space: agglomerative Hierarchical Cluster Analysis (HCA) using Ward’s method with Euclidean distance for building up dendrograms and Principal Component Analysis (PCA) using the Non-linear Iterative Partial Least Squares (NIPALS) method to compute principal components. Analytical data were first subjected to a pre-processing procedure by autoscaling.

RESULTS

Identification of classes and subclasses

The first step in the present study was the Principal Component Analysis (PCA) evaluation of the chemical composition data (for the selected elements, i.e. Sn, Rb, Pb, Fe, Ti, Ca, K, Al and Si) obtained from XRF analyses performed on the glazes of the porcelain objects.

Figure 3 shows the PCA scores and loadings plot which highlights a complete separation of the three manufactures. In particular, Vische and Vinovo manufactures are basically separated along the F2 axis, with the Vische production scattered on the positive part of the second principal component essentially distributed in the second quadrant of the plot and with Vinovo objects spread mainly around the origin and along the negative part of F2. Instead Rossetti and Vinovo production are separated along the F1 axis, with Rossetti manufacture forming a cloud along the positive part

of the first principal component. On the basis of these results the decorated jar (2260/c) identified in Table 1 as “Rossetti or Vezzi?” could be attributed to Rossetti production since the point corresponding to a Vezzi (Venice, Italy) object analyzed as counterproof falls in a completely different area of the PCA plot.

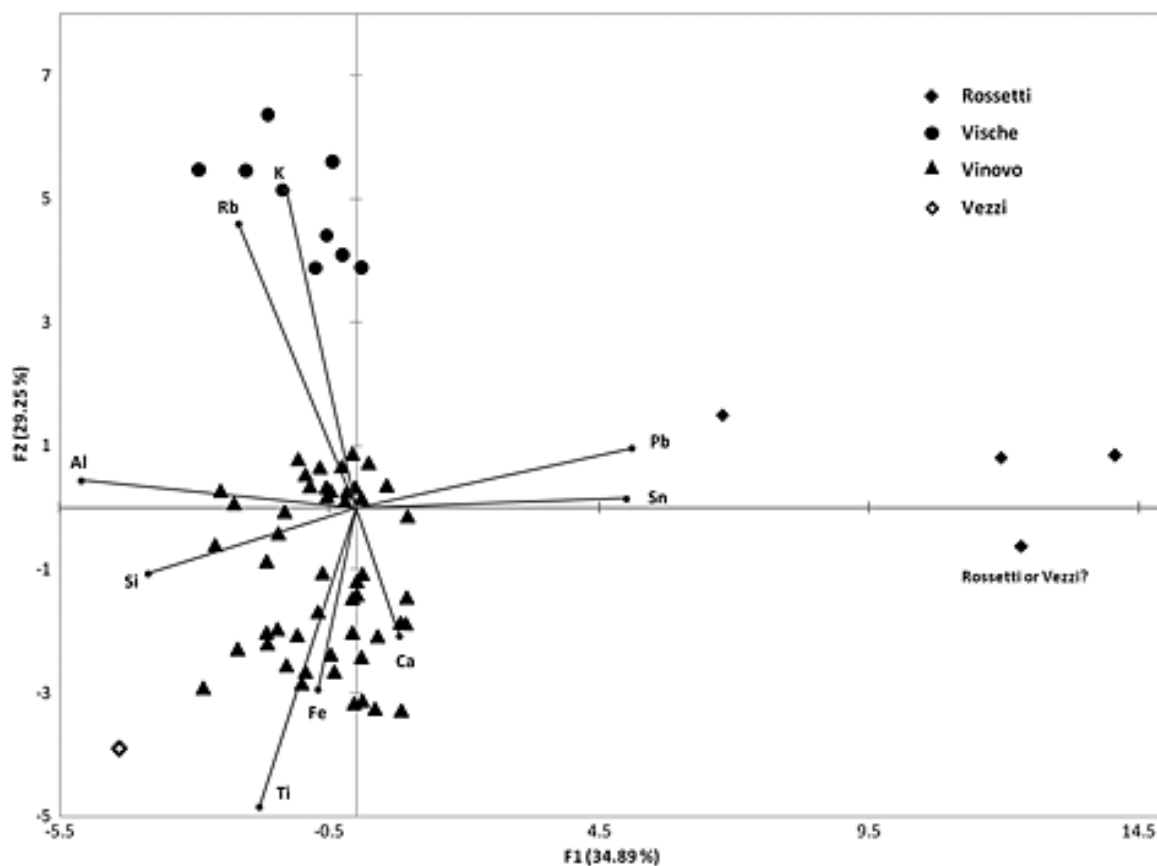


Figure 3: Principal Component Analysis score/loading plot obtained with the XRF data of the 9 detected elements on glazes of Vische, Rossetti and Vinovo manufactures and of the counterproof Vezzi object.

At last, from PCA evaluation based on the data of the glazes it is not possible to infer satisfying sub-classification in the cloud of Vinovo samples, where Hannong objects are not separated from the Gioanetti/Lomello production.

Vinovo manufacture phases were identified by a more typical approach, performing an agglomerative HCA on data from XRF analysis performed on the pastes. The HCA plot (Figure 4) identifies three subclasses. Based on definite assignments (i.e. signed, specifically marked or dated objects) two of them can be attributed to the Hannong period and the third one to the later Gioanetti and Lomello productions, which are indistinguishable from one another, as expected.

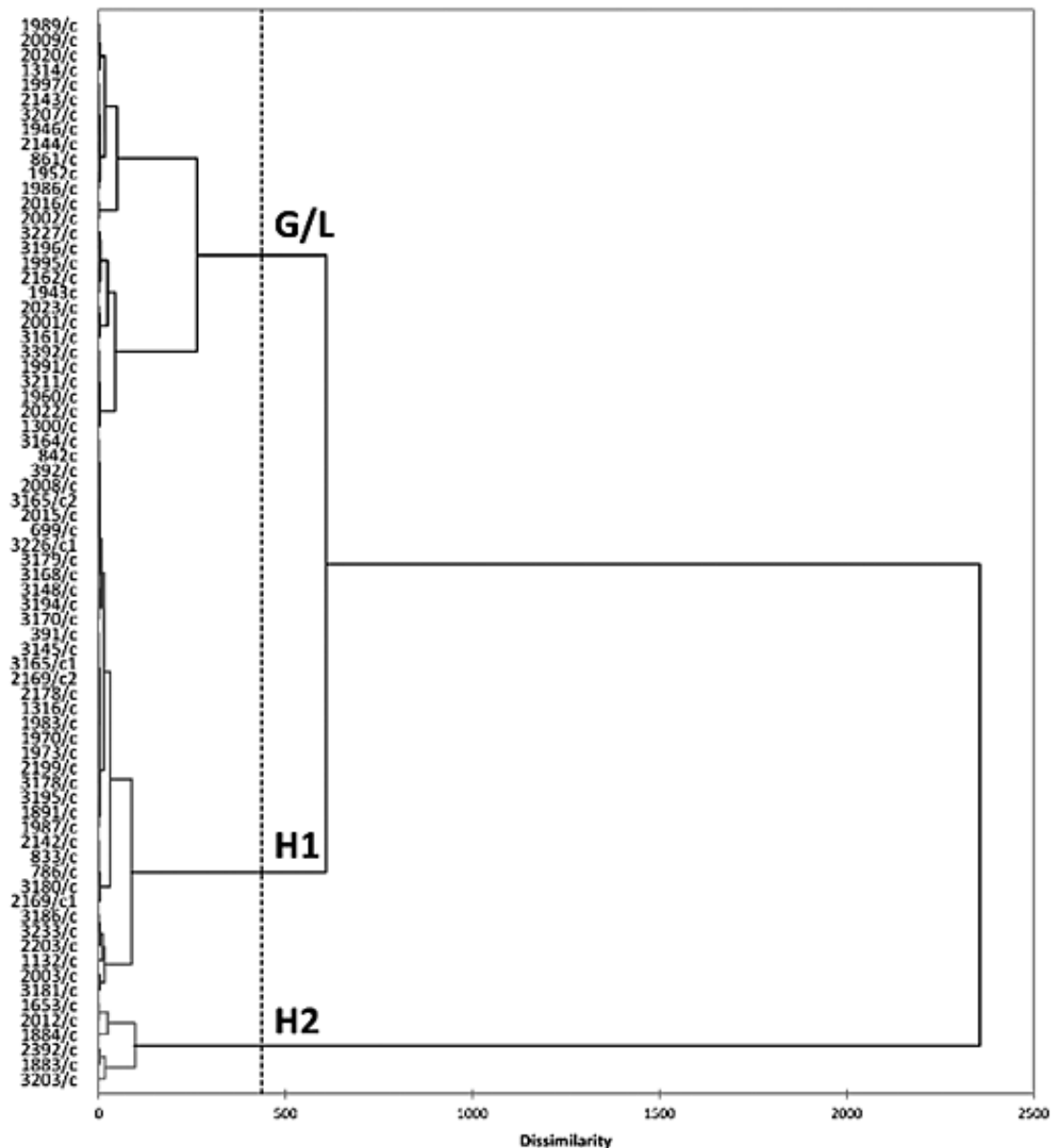


Figure 4: HCA plot obtained with the XRF data of the 9 detected elements on Vinovo pastes.

From now on the three classes will be indicated as H1 (the main Hannong production), H2 (Hannong alternative paste production) and G/L (Gioanetti/Lomello). H2 subclass consists of samples 1884/c (a decorated Athena figurine signed Mia), 3203/c (a soup tureen dated 1778), 2012/c (a biscuit vase, whose assignment to the Vinovo production was confirmed by the present work), 1653/c (a biscuit medallion), 1883/c (a white Athena figurine signed Mia) and 2392/c (a coffee pot). In greater detail the H2 group is well separated from the H1 and G/L classes, while these last two subclasses are less distinguishable, even with some probably wrong assignment (marked with a question mark in the “Scientific attribution” column, Table 1, attesting a lack of correspondence with the stylistic attribution or with particular identification features). On the basis of the H1 and G/L strong similarity, the assignment of the samples to one subclass or to the other

based only on the chemical composition should be regarded as not completely self-consistent. A specific mention must be made about the 1943/c piece, a *Scipione* biscuit figurine, whose stylistic attribution was uncertain between Vinovo (Gioanetti conduction) and Capodimonte (Naples, Italy). The comparison with the XRF results obtained on a similar Capodimonte biscuit figurine (catalogue number 2495/c) allowed a definitive assignment of this object to the Vinovo G/L subclass. Another peculiar piece is a signed DUBA lady with a hurdy-gurdy figurine (catalogue number 1974/c), originally assigned to the Vinovo manufacture but that did not match with any identified classes or subclasses (as outlier this object was excluded from HCA treatment). Finally, when no suitable areas for the paste analyses were available, the scientific attribution was made on the basis of the glaze composition and only “Vinovo” appears in “Scientific attribution” column of Table 1, without subclass details.

XRF chemical composition

XRF data, reported as mean weight % values of the 9 oxides detected in the pastes of the analyzed samples of the five classes/subclasses are illustrated in Table 2. Vische manufacture decisively differs from the other two productions for the very low SiO₂ content (46 wt%). Rossetti objects are characterized by the presence of Sn (0,28 SnO₂ wt%) and by the highest wt% of PbO (2,37) and K₂O (2,1).

Table 2: XRF paste mean composition, expressed as wt%, except for Rb₂O (ppm) for the five manufactures/subclasses.

	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	PbO	FeO	TiO ₂	SnO ₂	Rb ₂ O	Total
Vische	46	6,0	1,1	1,4	0,40	0,67	0,07	n.d.	31	56
Rossetti	84	5,2	1,9	2,1	2,37	0,55	0,05	0,28	48	97
Vinovo H1	66	5,9	0,9	0,9	0,02	0,63	0,08	n.d.	25	75
Vinovo H2	67	22,7	2,3	1,1	0,10	0,36	0,08	n.d.	30	94
Vinovo G/L	81	8,5	0,8	1,1	0,03	0,49	0,09	n.d.	37	92

The two H1 and H2 Vinovo subclasses differ from Vinovo G/L (and from Rossetti manufacture) for the lower SiO₂ content, while Vinovo H2 shows a very high Al amount (22,7 Al₂O₃ wt%) with respect not only to the other Vinovo productions but also compared to Vische and Rossetti. Moreover, a very important aspect can be pointed out observing the totals obtained summing the wt% of the 9 oxides. The results show that the total is particularly low for Vische manufacture (56 wt%), relatively low for Vinovo H1 (75 wt%), between 90 and 95 wt% for Vinovo G/L and Vinovo H2 and around 100 for Rossetti (97 wt%).

An explanation of this peculiarity can be found if we consider the limitation of the portable XRF instruments which allow the determination of the elements having $Z \geq 13$ and do not permit the detection of Na and Mg, which are usually typical components of porcelain pastes and glazes. In the present case this was expected as particularly relevant, at least for Mg and at least in the case of Gioanetti production, since from the historical literature (Figure 2) we know that raw materials containing high amounts of Mg were present in the recipes. To have at least an approximate esteem of the Mg quantity in the different productions and subclasses an XRF measure was performed with an He flow on a selection of objects. Analyses performed on the ceramic and clay standards containing < 1 wt% Mg gave a maximum inaccuracy of 20%, allowing a quite solid determination for this element.

The results are reported in Figure 5, which illustrates the MgO wt% of some selected samples from each class/subclass. From the diagram is immediately evident that Rossetti and Vinovo H2 show a very low Mg content, as expected from their higher total compositions. Vinovo G/L displays a medium Mg content -, followed by Vinovo H1 and Vische, which exhibit the highest Mg amount. This trend harmonizes well with the results obtained for the total wt%, constituting a relatively good complement to 100% for almost all the productions. The most remarkable exception is constituted by Vische manufacture. In this case even if we consider MgO and a reasonable amount of Na_2O , which for other XVIII century European manufactures reaches the maximum amount of 3,5 wt% (Gualtieri & Fabbri 2013; Freestone et al. 2003; Freestone 2000) the total is remarkably lower than 100%.

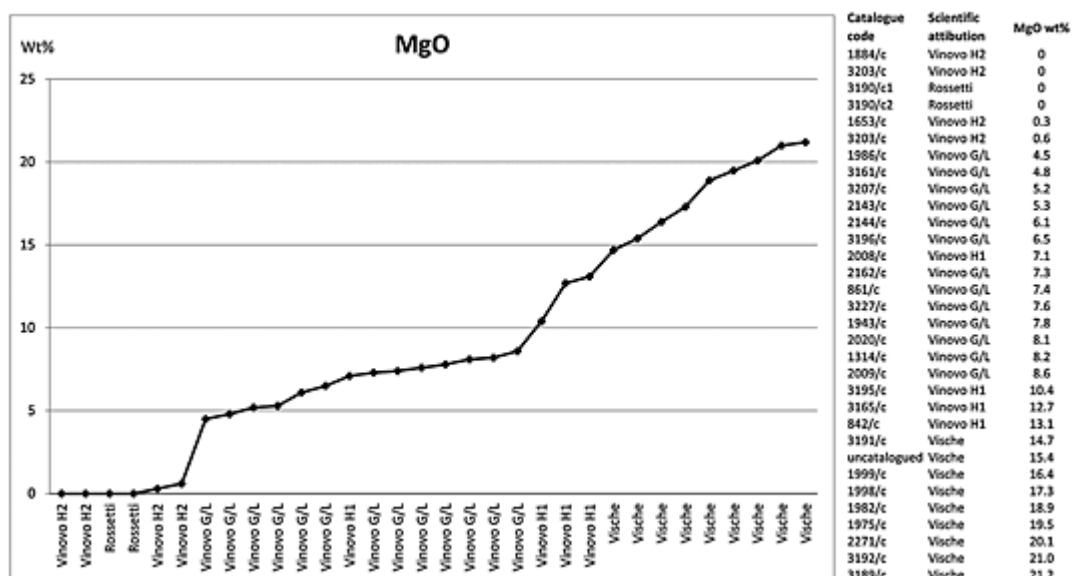


Figure 5: Diagram and table illustrating MgO wt% content of a selection of objects from all the manufactures/subclasses.

At last, XRF data, reported as mean weight % values of the 9 oxides detected in analyses performed on the glazes of the 5 classes/subclasses are illustrated in Table 3. These results can be easily examined observing the PCA plot showed in Figure 3: Rossetti manufacture shows the lowest SiO₂ wt% (58) value and a complete lack of Al₂O₃. Conversely, it exhibits a considerably high level of PbO (14,45 wt%) and the unique presence of SnO₂ (0,91 wt%). On the other hand Vische production displays the highest K₂O and Rb₂O contents (6,4 wt% and 101 ppm, respectively) and a not negligible amount of PbO (1,21 wt%). The correlation of K and Rb (see also Fig. 3) is evident for all the classes, and is ascribable to Rb substitution for K in feldspars. With respect to Vische and Rossetti, Vinovo manufacture shows higher Si, Fe and Ti and lower Pb contents. All the Vinovo subclasses and Vische production show Al content between 10 and 15 wt%. As for the total oxide wt%, the values range from 91 to 97 wt% except for Rossetti glazes which show a relatively low total of 77 wt%.

Table 3: XRF glaze mean composition, expressed as wt%, except for Rb₂O (ppm) for the five manufactures/subclasses.

	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	PbO	FeO	TiO ₂	SnO ₂	Rb ₂ O	Total
Vische	72	13,8	1,1	6,4	1,21	0,28	0,03	n.d.	101	95
Rossetti	58	n.d.	1,5	1,4	14,45	0,25	0,03	0,91	13	77
Vinovo H1	79	10,8	0,9	1,9	0,01	0,29	0,14	n.d.	38	93
Vinovo H2	75	12,3	1,1	1,2	0,03	0,36	0,15	n.d.	18	91
Vinovo G/L	82	11,9	0,8	1,6	0,03	0,36	0,16	n.d.	36	97

DISCUSSION

Glaze

One of the problems arising from the application of XRF analysis to surface layers, in the case of layered ceramic or porcelain objects, is related to the fact that if these layers are very thin, the exciting X-ray signal is able to cross them and reach the ceramic or porcelain body giving back a result that is the combination of the composition of the surface layer and of the paste (Casadio & Bezur 2009)). Other authors (Miao et al. 2012) seem confident in giving XRF data as pure glaze composition, without mentioning any contribution from the paste. The authors of the present paper agree with a possible influence of the paste composition depending both on the glaze thickness and on the atomic number of the analyzed elements. In the present case the glaze thickness was not measured for the lack of fragments available for a morphological evaluation, as mentioned above. Nevertheless the eventuality of a paste contribution on the glaze analysis does not seem to influence

the classification, as testified by the PCA diagram reported in Figure 3. This observation is particularly important due to the absence of areas suitable for paste analysis in several objects (typically when the base ring thickness is smaller than the XRF spot), which otherwise would have been excluded from the study.

Vische, Rossetti and Vinovo manufactures are well differentiated, as clearly emerged from the PCA score plot in Figure 3 and from Table 3. As for Vinovo production, the classification of the porcelain pastes in three subgroups (H1, H2 and G/L) observed from the HCA statistic treatment is not mirrored by a corresponding differentiation of the glazes. The only difference is a slightly higher Si content for Vinovo G/L, as already observed for the pastes. Vische glaze stands out for the peculiar contemporary presence of a moderate PbO amount and a high K₂O (around 6%) and a significant Rb (around 100 ppm) content, suggesting the use of a K-feldspar based flux. Meanwhile, taking into account the relative scarceness of scientific publications on the composition of the glazes of the European porcelain manufactures in the XVIII century, our data obtained on Vische glazes are nevertheless somewhat similar to Domoney (Domoney et al. 2012) results on Meissen pieces of the period 1725-1763 and to the glazes of two Meissen objects analyzed by Neelmeijer (Neelmeijer et al. 2014). On the other hand, for all the three Vinovo subclasses a Na-feldspar use as flux is conceivable due to the low K content, moreover justifying the lower total oxides wt%. These overall observation leads to suppose that for the three Vinovo subclasses and for Vische manufacture any significant technological innovation was adopted in the choice of raw materials and recipes, with respect to the generic composition of the glazes of the XVIII Century European hard paste porcelain.

Contrarily, Rossetti glaze, with a not detectable amount of Al and a relatively high PbO content bears no resemblance to a hard paste porcelain coating, but resembles to some extent a soft paste porcelain glaze (D'Albis 1997; Freestone et al. 2003). On the other hand, Rossetti glaze shows the presence of Sn, thus resembling a peculiar adaptation of the tin-opacified lead-alkali glazes described by Tite (Tite et al. 1998) for several ancient pottery and for XIII-XVI Centuries Italian majolica. In this case the presence of a certain amount of Na in Rossetti glaze could be predictable and would partially account for the low total (77 wt%). This glaze composition would also find a possible explanation in a technological continuity with the Rossetti majolica manufacture, which had forerun the porcelain production, as underlined by Fabbri for the Capodimonte manufacture (Amato et al. 2009; Fabbri & Gualtieri 2015).

Paste

One of the more stimulating issues of the present work was to look for a compositional

differentiation between the various phases of Vinovo manufacture, from the Hannong period to Gioanetti (and Lomello) production. This classification should have been quite trivial, since it is known from the most important historical reference that Gioanetti paste is very peculiar (“toute particulière”) (Brongniart 1844, vol II, p. 423) and thus it was expected to be well distinguished from the Hannong production. In particular, an original letter sent from Gioanetti to Brongniart on the 21st of august 1807, together with some trunks containing raw materials and porcelain objects, is stored in Sèvres archives. In this letter Gioanetti describes his main paste recipe: 20 parts of quartz, 20 parts of Baldissero magnesite, 20 parts of fired porcelain, 6 parts of refined Barge clay and 4 parts of Frossasco feldspar. In turn, the fired porcelain was obtained by: 20 parts of quartz, 10 parts of Baldissero magnesite, 5 parts of refined Barge clay and 4 parts of Frossasco feldspar (Maritano, in press). These recipes would have suggested high contents of Si and Mg in the porcelain bodies and a relatively low Al amount, in comparison with the composition of the traditional porcelain obtained with kaolin rich recipes.

Instead, peculiar results were observed. First of all, Vinovo manufacture of the Hannong H1 and Gioanetti/Lomello periods are slightly differentiated by HCA and their composition is very similar, especially if compared to the much more distinguished H2 group (Table 2). In particular, group H2 differs from the other two Vinovo manufacture subclasses (and also from Vische and Rossetti production) due to the relatively high Al content that makes this subclass more similar to other important European manufacture, such as Meissen and Du Paquier (Neelmeijer et al. 2014; Gualtieri & Fabbri 2013; Casadio & Bezur 2009). One of the hypothesis for this outcome is that imported kaolin was used by Hannong in the making of the most precious objects (H2) where he was probably reproducing a formulation that resembled the composition of hard paste porcelain that, as French archaist, he should have known pretty well. Notwithstanding the SiO₂/Al₂O₃ ratio is higher compared with the above mentioned Central European manufactures, suggesting a relatively lower kaolin content. On the other hand, for the rest of the production (H1) he adopted an alternative recipe making use of local raw materials.

At this regard, the evidence emerged from Mg measure finds a clear explanation: our data definitely show that Mg containing minerals were not a novelty introduced by Gioanetti, but they were certainly already present in large quantity in the Comte of Vische secret recipes and also in the Hannong H1 formulation. All these consideration lead to the conclusion that Mg based pastes were the path chosen by all the Piedmontese manufactures in the second half of the eighteenth century. These evidences find support in recently acquired archive documents reporting the use of ‘*terra di Baldissero*’ by Hannong and of ‘*magnesia carbonata*’ by the *Conte Sale di San Martino* (Vische) (Maritano, in press). Brongniart analyses on Gioanetti Baldissero magnesite (Figure 6) confirms

that Mg source was essentially the same $MgCO_3$ for both Vische and Vinovo directorship.

Magnésite de Vallecas, près Madrid. . . .	Silice.	Magnésie.	Eau.
	54	24	20
Giobertite (ou carbonate de magnésie, de Baldissero a Castellamonte, près Turin.	Acide carbonique.	Magnésie.	Eau.
	49	48	3
Elle est presque toujours mêlée de silicate de magnésie.			

Figure 6: Composition of the Baldissero magnesite as analyzed by Brongniart (1844, vol. I, p. 70).

The very low total oxides wt% observed for Vische manufacture could be presumptively explained by a high porosity of the material. The low analysis totals (as low as 70%) due to a high microporosity are well known in the scientific literature (Freestone 1982) for ancient ceramic materials. The presence of a certain degree of microporosity is reported in the literature also for porcelains (Zucchiatti et al. 2008) and its influence on the totals should be carefully scrutinized. On the other hand, in the present work a normalization to 100 wt% (as suggested by Freestone) is not possible, due to the fact that the determination on Mg is only semiquantitative and Na is totally not detectable with the used instrumentation.

On the other hand, Rossetti porcelain production did not make use of this kind of formulation and at the same moment it does not even resemble Du Paquier manufacture (Al_2O_3 is around 5 wt% in Rossetti objects vs. 34-38 wt% of the Du Paquier manufacture and SiO_2 is 84 wt% vs. 55-59 wt% (Casadio et al. 2012)), as could be hypothesized on the base of the presence of Jakob Helchis, from the Vienna plant, as archanist. Notwithstanding the very limited number of Rossetti porcelain objects in the Palazzo Madama collection, our data are in very good agreement with the composition reported by Freestone on a Rossetti figurine from the British Museum (Freestone et al. 2003). In particular SiO_2 (83.0 wt% from Freestone paper vs. 84 wt% from the present work), Al_2O_3 (5.9 wt% vs. 5.2 wt%), CaO (1.8 wt% vs. 1.9 wt%) and FeO (0.7 wt% vs. 0.55 wt%) show a perfect correspondence. As for SnO_2 (0.28 wt%) and PbO (2.37 wt%) detected amounts the intentional addition of Sn for whitening purpose and an unintentional contamination of Pb pending the manufacturing (or firing) step are plausible (Fabbri et al. 2014). In the end, this composition suggests that all the examined Rossetti pieces are soft paste porcelain.

CONCLUSIONS

The present work demonstrated the reliability of the portable XRF technique in the *in situ* examination of the three XVIII century Piedmontese porcelain manufacture. Rossetti, Vische and Vinovo productions were clearly discerned on the basis of analyses performed on glazed areas. On the other hand, the distinction of the different conductions of the Vinovo manufacture was slightly evidenced only by the HCA treatment of paste composition data. HCA evidenced the presence of three subgroups: two attributed to the Hannong production (H1 and H2) and a third to the Gioanetti and Lomello conductions (G/L). H1 and G/L were fairly separated, while the H2 group is very well differentiated. The evaluation of the H2 class mean chemical composition strongly suggest a kaolin-based alternative recipe for the most precious Hannong objects, even if the kaolin content would presumably have been lower than for the typical Central European hard paste porcelains. Particular attention has been paid to the magnesium abundance in the paste, which should have been the feature of Gioanetti manufacture according to Brongniart. XRF reading on magnesium performed with portable instruments should be regarded with caution, nevertheless analyses performed in He clearly revealed that in the previous Vische manufacture and Vinovo Hannong conduction (limited to the H1 formulation) Mg was even more abundant. These results definitely confirmed that the introduction of Mg-based raw materials in the porcelain composition, historically attributed to Gioanetti, was ascribable at least to the Conte Birago of Vische. Later on the same solution was adopted also by Hannong and by Gioanetti, who refined the recipe obtaining better aesthetic results. The historical attribution to the Piedmontese doctor and chemist of the new formulation was probably ascribable not only to Gioanetti scientific and social prestige, but also to the veil of secrecy that usually surrounded porcelain European manufactures in the XVIII century. On the other hand, not all the questions found a specific answer. For example, as far as Rossetti manufacture is concerned, the results suggest that none of the analysed objects is made of hard paste porcelain. Nevertheless the assignment of a fourth piece to the Rossetti collection of the Palazzo Madama Museum, the very limited number of examined pieces does not allow to draw definitive conclusions about this manufacture and highlights the need to extend the study to a greater number of samples.

ACKNOWLEDGEMENTS

The authors would like to thank Prof. Ian C. Freestone for the supporting information.

REFERENCES

- Amato, F. et al., 2009. Caratteristiche tecnologiche delle porcellane capodimonte (Napoli, metà XVIII sec.). In *Le classi ceramiche: situazione degli studi. Atti della 10a Giornata di Archeometria della Ceramica*. Bari: Edipuglia, pp. 169–187.
- Bezur, A. & Casadio, F., 2009. A scientific evaluation of the materials. In *Fired by passion. Vienna baroque porcelain of Claudius Innocentius Du Paquier*. Stuttgart: Arnoldsche Art Publishers, pp. 1165–1203.
- Brongniart, A., 1844. *Traité des arts céramiques ou des poteries, considérées dans leur histoire, leur pratique et leur théorie*, Paris: Bechet Jeune ; Mathias.
- Brosio, V., 1973. *Rossetti Vische Vinovo. Porcellane e maioliche torinesi del Settecento*, Milano: Görlich Ed.
- Casadio, F., Bezur, A., Domoney, K., Eremin, K. Lee, L., Mass, J. L., Shortland, A., Zumbulyadis, N., 2012. X-ray fluorescence applied to overglaze enamel decoration on eighteenth- and nineteenth-century porcelain from central Europe. *Studies in Conservation*, 57(s1), pp.S61–S72. Available at: <http://www.maneyonline.com/doi/abs/10.1179/2047058412Y.0000000047>.
- D’Albis, A., 1997. Making Soft Past in the XVIII Century. *Key Engineering Materials*, 132-136, pp.1432–1433.
- Domoney, K., Shortland, A.J. & Kuhn, S., 2012. Characterization of 18Th-Century Meissen Porcelain Using Sem-Eds*. *Archaeometry*, 54(3), pp.454–474. Available at: <http://doi.wiley.com/10.1111/j.1475-4754.2011.00626.x> [Accessed October 20, 2014].
- Fabbri, B. & Gualtieri, S., 2015. Capodimonte porcelain: Glaze composition and its technological implications. *Ceramics International*, 41(2), pp.2318–2327. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0272884214015648> [Accessed January 20, 2015].
- Fabbri, B., Gualtieri, S. & Amato, F., 2014. Capodimonte porcelain: A unique manufacture. In M. MartínónTorres, ed. *Craft and science: International perspectives on archaeological ceramics*. Doha, Qatar: Bloomsbury Qatar Foundation, pp. 117–124. Available at: <http://dx.doi.org/10.5339/uclq.2014.cas.ch13>.
- Freestone, I.C., 1982. Applications and potential of electron probe provenance investigations of ancient ceramics. *Archaeometry*, 24(2), pp.99–116.
- Freestone, I.C., 2000. The science of early British porcelain. In *International Ceramics Fair and Seminar*. pp. 19–27.
- Freestone, I.C., Joyner, L. & Howard, R., 2003. The Composition of Porcelain from the Isleworth Manufactory. *English Ceramic Circle Transaction*, 18, pp.284–293.
- Gualtieri, S. & Fabbri, B., 2013. Indagini archeometriche sulla porcellana di Capodimonte e criteri base per una classificazione delle porcellane. In *Fonti storico tecniche della porcellana*

italiana. *Atti della 14a Giornata di Archeometria della Ceramica*. Faenza: Valfrido, pp. 119–136.

Malaguzzi, F., 1987. I «segreti» della Manifattura di porcellana di Vinovo : indediti di Vittorio Amedeo Gioanetti negli archivi di Sèvres. In *Bollettino della Società piemontese di archeologia e belle arti*. pp. 91–103.

Maritano, C., La Regia Fabbrica delle Porcellane di Vinovo (1776-1825): la storia, gli artisti. In *Fascino e splendore della porcellana in Piemonte Rossetti, Vische, Vinovo 1737-1825*. In press.

Miao, J.-M. et al., 2012. Non-Destructive Analysis of “Original” Song Dynasty Guan Wares and Later Imitations From the Palace Museum Collections, Beijing. *Archaeometry*, 54(6), pp.955–973. Available at: <http://doi.wiley.com/10.1111/j.1475-4754.2012.00669.x> [Accessed October 23, 2014].

Neelmeijer, C., Pietsch, U. & Ulbricht, H., 2014. Eighteenth-Century Meissen Porcelain Reference Data Obtained By Proton-Beam Analysis (PIXE-PIGE). *Archaeometry*, 56(4), pp.527–540. Available at: <http://doi.wiley.com/10.1111/arcm.12050> [Accessed October 23, 2014].

R Core Team (2013), R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL <http://www.R-project.org/>.

Rousseau, R.M., 2001. Concept of the influence coefficient. *The Rigaku Journal*, 18(1), pp.8–21.

Van Espen, P., 2000. ED-XRF spectrum evaluation and quantitative analysis using multivariate and non linear techniques. *JCPDS*, 43, pp.560–569.

Zucchiatti, A., Pascual, C., Ynsa, M.D., Castelli, L., Recio, P., Criado, E., Valle, F.J., Climent-Font, A., 2008. Compositional analysis of XVIII century glazed, polychrome, layered porcelain by non-destructive micro α -PIXE. *Journal of the European Ceramic Society*, 28(4), pp.757–762. Available at: <http://linkinghub.elsevier.com/retrieve/pii/S0955221907004918> [Accessed October 19, 2014].