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▶ To cite this version:

Philippe Colomban, Gulsu Simsek. pXRF study of pottery: State of the art and perspectives. TECH-NART 2019 – International Conference Non-destructive and microanalytical techniques in art and cultural heritage, May 2019, Bruges, Belgium. hal-03964390

HAL Id: hal-03964390 https://hal.science/hal-03964390v1

Submitted on 31 Jan 2023 $\,$

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Portable XRF study of pottery: State of the art and Perspectives

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Although portable/handheld X-ray Fluorescence instruments are available from decades, the number of publications reporting on-site analysis of pottery remains very limited. Most of them have been focused on the paste composition and not the (glazed) décor, which is the most advanced part from the technological and aesthetical point of view.

Ceramic approach

- Elemental characteristics of Flux (K, Na, Pb, Ca: feldspar, marl), clays (Al) and Si content; characteristic traces (Bi, Zr, REE)

- Impurities tracing the process (purification) and origin (Fe, Ti, Zr, REE)

- Characteristics of trace and second phases related to rare ores

Algorithmic approach

- Biplots & Ternary diagrams of major, minor and traces elements

- Principal Component Analysis

Ti vs. Fe

Delft

- Dendrograms built with selected/non selected data

Advantages & Drawbacks

On-site analysis and selection of artefacts Fast collection of data (a few *minutes/spot*) ⇔ *higher number* of objects, statistics ... Many instruments available



Light elements and some traces not measured (B, C, O, N, Na)

Semi-quantitative (specific calibration) Difficulty to determine the analyzed *volume (variable depth)*

Contact Positioning and analyzed surface depend on object

Discrimination between genuine stonewares and fakes (Meissen, Delft, China, etc.) Boccaro wares: « copies » of Yixing wares



Bodies analyses by XRF Elements related to clays and sands



Procedures

Representative case studies

1) At the Museum storage rooms

	Brongniart' porcelain
8 -	
body	Chemometrics : Euclidia

Zr/Si – Rb/Si – Sr/Si

n distances ie most representative criteri

shape

device emission: Direct mainly directional

Secondary emission of the sample: all directions !

Depending on system / measuring conditions :

Different national legislation

Measurement configuration is *important!* (*safety*)

2002-2019

pXRF Application Areas



Obsidian (origin, trade) 74 Bronze (technology) 18 Glass bead (origins, trade) 6 Pottery (origin, technology) 48 Prehistoric tools 11 Paintings 19 Frescoes 2 Rock art 8 Mortars & plasters 3 Gems 1 Gilding (technology) 7 Coins 2 Musical instruments 1 Stones (origins) 10 Metal residues (Technology) 5 Fossils 2 Glazes & enamels 22

etc

Examples of recent works: 2018-2019

Research Material	First Author	Date	pXRF model	Complementary Instruments
Iznik Tile	Simsek, G.	2019	Hitachi X-Met8000 Expert Geo	Not used
Soil	Ruano, S.M.	2019	Thermo Niton XLT 792	ICP-MS
Alluvium & Rock	Groover, K.D.	2019	ED-XRF DP-4000 Delta	WD-XRF
Soil	Kim, H.R.	2019	Olympus Innov-X	ICP-AES
Mine	Rincheval, M.	2019	Olympus Innov-X	WD-XRF
Nutrition	Fischer, S.	2019	Bruker Tracer 5i	Organic analyzer, ICP- OES
Wall Paint	Ericson, B.	2019	Niton XL3t & Olympus Delta Classic Plus	AAS
Plant	Sapkota, Y.	2019	Bruker Tracer III-SD	ICP-MS
Soil	Chakraborty, S.	2019	Olympus DP 6000	Not used
Soil	Rawal, A.	2019	Vanta	Not used
Obsidian	Ladefoged, T. N.	2019	Not documented	Not used
Mine	Simpson, M. P.	2019	Not documented	XRD, SEM
Soil	Ericson, B.	2019	Olympus Innov-X	Not used
Chinese Porcelain	Xu, W. P.	2019	Thermo Niton XL3t GOLDD+	Not used
Teeth	Hammond, A. S.	2019	Bruker Tracer III	Not used
Sculpture	Fort, R.	2019	Thermo Niton XL3t GOLDD+	Not used
Soil	Padilla, J.T.	2019	Olympus DP 4000 Delta	Not used
Drill core (Mining)	Duee, C.	2019	Thermo Niton XL3t 980 GOLDD	pIR, XRD, Raman
Mine	Hollis, S. P.	2019	Olympus Innov-X	Not used
Mudbrick	Lorenzon, M.	2019	Olympus Innov-X	SEM-EDS
Fresco Paint	Khranchenkova, R.	2019	Bruker Tracer S1-Turbo	Not used
Soil	Rogan, G.	2019	Bruker Tracer III-SD	ICP-OES
Metal Brooch	Roxburgh, M.A.	2019	Thermo Niton XL3t GOLDD	Not used
Sediment	Rashid, H.	2019	Not documented	lsotope ratio mass spectrometer
Ceramics	Shalvi, G.	2019	Bruker Tracer III-V	EPMA, LA ICP-MS
Granite	Steiner, B. M.	2019	Olympus DP 6000	ICP-MS
Sediment	Hines, B. R.	2019	Olympus Innov-X Delta	ICP-MS, fusion XRF
Soil	Xu, D.	2019	Thermo Niton	LIBS, vis-NIR, mid-IR
Soil	Oyourou, J.N.	2019	Thermo Niton XL3t GOLDD+	ICP-OES
Soil	Gutiérrez-Rodriguez, M.	2019	Thermo Niton XLt 792	SEM
Coin	Ortega-San-Martin, L.	2019	Bruker Tracer III-SD	AAS
Mine	Turner, O.	2019	Olympus Delta X	ICP-AES/MS
Lithology	Yarbrough, L. D.	2019	Bruker Tracer IV-SD	Not used
Pigments in ceramics	Obregon, C. L.	2018	Olympus DP 6000-CC	Not used
Polluted water	Zhou, S.	2018	Thermo NitonXL3t 950	Lab. Type XRF
Soil	Caporale, A. G.	2018	Olympus Delta X	ICP-MS
Soll	Harvey, P.J.	2018	Olympus Innov-X	Not used
Carbonates	Sinnesael, M.	2018	Bruker Fracer IV	μ-XRF
Sediment	Kincey, M.	2018	Thermo Niton XLt 792	ICP-OES
Obsidian	Abedi, A.	2018	GOLDD+	Not used
Obsidian	Frahm, E.	2018	Olympus Vanta M	Bench-top EDXRF, NAA
Ceramic	Niziolek, L. C.	2018	Olympus Innov-X Alpha	Not used
Mine	Сао, Ү. Н.	2018	Thermo Niton XL3t GOLDD+	Bench-top SEM
Pottery	Scott, R. B.	2018	Bruker Tracer III SD	Lab type XRF, ICP-OES
Soil	Godinho, S.	2018	Bruker S1 Titan 600 LE	XRD
Soil	Dos Santos Teixeira, A. F.	2018	Bruker S1 Titan LE	Not used
Mineral (quartz)	Desroches, D.	2018	Thermo Niton XL3t GOLDD+	Lab type XRF
Mortar & Plaster	Tenconi, M.	2018	Thermo Niton XL3t GOLDD+	SEM-EDS
Petroglyph	Macholdt, D. S.	2018	Thermo Niton XL3	Not used
Soil	L Harvey, P. J.	2018	L Olympus Delta Premium	l Not used

The Art Institute of Chicago (7) Private US collection (19) Sèvres artefacts : secure origin,

Musée National, Sèvres (45)

rchased/exchanged with Sèvres Factory/museum by A. Brongniart, beginning of 19th century





++ Chines Fe/Si \Rightarrow 18th Meissen exhibit variations but \neq 20th / Chinese / others ⇒ Some pieces misclassified

AA AIC



G. SIMSEK, F. CASADIO, Ph. COLOMBAN, K. FABER, L. BELLOT-GURLET, G. ZELLEKE, V. MILANDE, E. MOINET On-site identification of earlier Meissen Böttger J. Am. Ceramic Society 97 [9] (2014) 2745-2754

Chinoiserie style

lestroved Palace

on Iznik tiles ovation for Edirne



Studying early European porcelain ("China") production from Meissen (Saxony/Gernany) created by Ehrenfried Walther vonTschirnhaus & Johann Friedrich Böttger

1706: Stoneware experimentation and production. 1708: The Steinbäckerei first established at Dresden 1708: Böttger makes hard paste porcelain for the first time. 1710: Augustus the Strong founds the Meissen Factory. 1714: Stoneware production declines because of cost, taste

> G. SIMSEK, Ph. COLOMBAN, F. CASADIO., L. BELLOT-GURLET, K. FABER, G. ZELLEKE, V. MILANDE, L. TILLIARI analysis J. Am. Ceramic Society 98[10] (2015) 3006-3013.

2) On-site : building walls Origin of Iznik tile technology – International Timurids style

Edirne mosques **Unesco World Heritage**





between 16th and 17th-c. Iznik tablewares

Muradiye (1435-1436): Coloured glazed tiles related to Timurid and Seliuk heritaae

Muradiye: (<1436?) Blue-and-white tiles, very specific production connected to U

Sah Melek Pasa (1429): Similar to uradiye's coloured glazed tiles Earlier period of Uc Serefeli (1410-1447) Close to B&W Iznik production: tiles of Muradi 14th-15th centuries Red body, lead-alkali glaze

with high Sn Yeşilce (1442): Different, linked to Seljuk and Timurid production

Classical period of Iznik production 16th century Fritware/Stonepaste, lead-alkali alaze with medium Sn content

B7-8

Late period of Iznik production 17th century lead-alkali glaze with no Sn







Dendrograms: Better interpretation of the results by social scientists (archaeologists, art historians, etc.,

First on-site, non-invasive analyses of the tiles excavated at Iznik tile kilns, carried out with a pXRF instrument



Décor analyse by XRF Glazes are mainly Pb based:

highly problematic for XRF (semi-)quantification not possible to go beyond qualitative statements



Easy discrimination between genuine Böttger productions from other ones (including fakes) is possible. A variety of gilding techniques, some of them without gold

Conclusions

Ethical rules of cultural heritage studies now limit destructive analyses as much as possible.

Therefore, the portable, non-destructive techniques, e.g. pXRF, pRaman, and FORS have become essential tools for the analyses of the objects in place or exclusive objects preserved in the secure rooms of museums or private collections.

Thus, a methodology must be created to make the analytical procedures more reliable when using portable instruments.



V.A.S.T

67 Iznik tiles attributed to the production from 14th- to 17th-c.from Iznik Tile Kiln Excavations, Iznik (25) • Muradiye Mosque, Edirne (9) Sah Melek Paşa Mosque, Edirne (4) •Yeşilce Mosque, Edirne (2) ·Üç Şerefeli Mosque, Edirne (9) ·Selimiye Mosque, Edirne (18)



Group #

1-14th-15th-c. productions: low SiO2 high Al2O3 2- 16t-17th-c. productions: high SiO2 low Al2O 3- 16th-17th-c. productions: medium SiO2 low Al2O3 high CaO

0.05 0.06 PbO / SiO₂

Analysed artefacts

Pb + K + Bi + Na

High amount of network formers

= higher firing T. > 800-900 °C

Sodium in the glaze can not be measured with pXRF but can be calculated by the amount remaining after the subtraction of the sum of the other oxides from 100.

92/10

G. SIMSEK. O. UNSALAN. K. BAYRAKTAR. Ph. COLOMBAN Consite pXRF analysis of glaze compos Edirne mosques (15th and 16th-centuri Ceramics International 45[1] (2019) 595 g agents of "Iznik" tiloe

G. SIMSEK, B. DEMIRSAR ARLI, S. KAYA, Ph. COLOMBAN On-site pXRF analysis of glaze, body composition and colo Enik tile kins excavation J. Eur. Ceram. Soc. 39[6] 2019 2199-2209.

3) Measurement at excavation site Discrimination between Chinese (Yunan) and Vietnamese porcelains with similar decor

confirmation for 9 samples wrong' assignment for 2 samples 2 samples un assigned ⇒Yunnan productions ? Chinese Hong River Ming exportation ban for official/major kilns: 14th century \Leftrightarrow > mid 14th c. large exportation of Vietnamese productions (Hai Dung Province). Rather similar productions found in Fujian, Hunan, Guangxi,

Ch: Chinese ware C: celadon or monocolor shards BW: blue-and-white shard BI: Brown and Ivory IB: Iron brown painting stonewa MC: multicolor ward Ly: Ly Dynasty ware, Hanoi citade HL: Ha Lan kiln ware CD: Chu Đâu kiln ware KQ: Ngu Hanh Son ware JP: Japan ware Viêt-2 Kor: Korea Goryo ware BT: Bat tràng kiln ware Clay/Kaolin: from Chu Đâu excav G. SIMSEK. Ph. COLOMBAN. S. WONG. B. ZHAO. A. ROUGEULLE. N.Q. LIEM J. Cultural Heritage 16 [2] (2015) 159-172. Ath-16th c A. ROUGEULLE, H. RENEL, G. SIMSEK, Ph. COLOMBAN ceramic production at Qalhàt, Oman, inar for Arabian Studies, Suppl. 44 (2

Easy pXRF differentiation between Chinese and Vietnamese productions From Zr, Rb and Sr content ⇔ Use of different clays



(free & innovative design) from Vietnam? (blue overglaze painting, Mn-Fe-rich cobalt, 'chocolate' bottom)

Guangdong and Yunnan Provinces, closes to Vietnam

Are all porcelains with Vietnamese style décor