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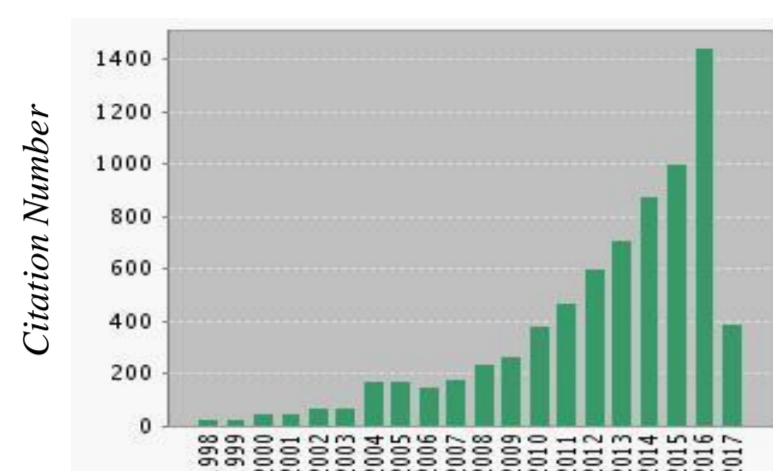
Portable XRF study of pottery: State of the art and Perspectives

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Aim



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 aesthetic point of view.

Procedures

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
- Dendrograms built with selected/non selected data

Advantages & Drawbacks

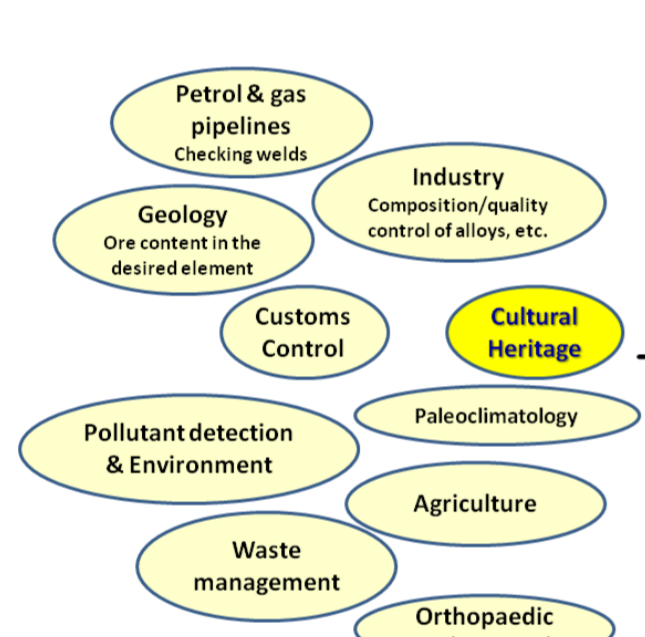
On-site analysis and selection of artefacts
Fast collection of data (a few minutes/spot) ⇔ higher number of objects, statistics ...
Many instruments available



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 shape
Direct device emission: mainly directional
Secondary emission of the sample: all directions!
Depending on system / measuring conditions:
Different national legislation
Measurement configuration is important! (safety)

pXRF Application Areas

2002-2019



- 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.

Representative case studies

1) At the Museum storage rooms 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

Ti vs. Fe

K vs. Ca

Decor analyse by XRF
Gildings: Various contents of Au / Cu / Hg - aesthetic? - techniques?

Studying early European porcelain ("China") production from Meissen (Saxony/Germany) created by Ehrenfried Walther von Tschirnhaus & 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.

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

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

**Erdine mosques
Unesco World Heritage**

Glaze and colouring agents measured at Erdine mosques

Body, glaze and colouring agents measured at Iznik Tile Kiln Excavations

Selimiyeh (1569-1575): Intermediate between 16th and 17th-c. Iznik tilewares

Muradiye (1435-1436): Coloured glazed tiles related to Timurid and Seljuk heritage

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

Sah Melek Pasa (1429): Similar to Muradiye's coloured glazed tiles

Red body, lead-alkali glaze with high Sn

Yedigöze (1442): Different, linked to Seljuk and Timurid production

Classical period of Iznik production: 16th century Fritware/Stoneware, lead-alkali glaze with medium Sn content

Late period of Iznik production: lead-alkali glaze with no Sn

High amount of network formers = higher firing T. > 800-900 °C

67 Iznik tiles attributed to the productions from 14th- to 17th-c. from Iznik Tile Kiln Excavations, Iznik (25) Muradiye Mosque, Erdine (9) Sah Melek Pasa Mosque, Erdine (4) Yedigöze Mosque, Erdine (2) Üç Serefeli Mosque, Erdine (9) Selimiyeh Mosque, Erdine (18)

Body analyses of the tiles from Iznik Tile Kiln Excavations: 1- 14th-15th-c. productions: low SiO2 high Al2O3, 2- 16th-17th-c. productions: high SiO2 low Al2O3, 3- 16th-17th-c. productions: medium SiO2 low Al2O3, high CaO

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.

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

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 assigned
• Yunan productions? Chinese Hong River

Ming exportation ban for official/major kilns: 14th century ⇔ mid 14th c. large exportation of Vietnamese productions (Hai Dung Province)

Rather similar productions found in Fujian, Hunan, Guangxi, Guangdong and Yunan Provinces, closes to Vietnam
Are all porcelains with Vietnamese style décor (free & innovative design) from Vietnam?
(blue overglaze painting, Mn-Fe-rich cobalt, 'chocolate' bottom)

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

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.