Article

On-Site Identification of Pottery with pXRF: An Example of European and Chinese Red Stonewares

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Abstract: The invention of European hard porcelain, which aims at imitating kaolin-containing white paste of Chinese porcelain, had been started by the development of the technology of "red porcelain", so-called "*Jaspisporzellan*" by Johann Friedrich Böttger in the early-eighteenth century at Meissen (Saxony). The visual features of the earlier Böttger red stoneware were rather similar to the one produced in Yixing, China. The prominence of Böttger productions allowed the manufacturing to be expanded across Europe to different countries (Holland, England, France, etc.). In this study, the chemical characteristics of nine European unglazed objects produced in England, France, Russia, and Holland from the 17th to 19th century and 10 Chinese (unglazed or enameled) red stoneware have been studied by using an on-site characterization technique pXRF. The results were compared with the previous studies carried out on 25 unglazed, polished, and non-polished Böttger artefacts. This non-invasive, speedy technique allows a methodology to be created for distinguishing the technological differences related to the provenance and authenticity of the artefacts. The elemental measurements explicitly show the significant discrepancy of Dutch objects from the main group, which involves other European and Chinese ones. Both a Lambertus van Eenhoorn (Delft) statue and an Ary de Milde (Delft) teapot are distinguishable from other European red stoneware by the high content of iron and calcium and high content of titanium and potassium, respectively, found in their body compositions. An overall comparison was made between the measurements made at different times in order to evaluate the error range arising from the measurement procedure (e.g., energy resolution of other series of the same instrument model).

Keywords: stoneware; Europe; composition; pXRF; 17th–18th centuries; China; Ary de Milde; Böttger; Lambertus van Eenhoorn

1. Introduction

Even today, the identification of works of art mostly follows the senses of the connoisseur rather than a scientific point of view: the shape and texture of the object, color, aesthetics of the decor, weight in hand, sound after a slight shock, etc. It follows that the conclusion is highly subjective, if not an authoritative argument. The first scientific studies in history were performed at the beginning of the 18th century by the French scientist, Ferchault de Réaumur [1–4]. For a long time, at least until the 1950s, the method of analysis required the (partial) destruction of the pottery artwork [5], and even today, all the characterization techniques used remain micro-destructive and are carried out in the laboratory [6–8]. Since the beginning of the 2000s, the performance of mobile devices, namely Raman micro-spectrometer [9–16] and portable X-ray fluorescence (pXRF, Table 1) [15–38], has enabled on-site analyses of cultural heritage objects and materials in an attempt to answer the questions regarding the elementary and molecular composition and, thus, to apprehend questions relating to the place of production, authenticity, technology, exchanges, etc. The data in Table 1, which shows a survey published in a preliminary conference presentation [37], are certainly not exhaustive but show the incremental use of pXRF devices in

the characterization of archaeological materials and cultural heritage objects. The intrinsic weaknesses of the method (weak positioning control on uneven surfaces, impossibility of measuring light elements (B, Li, Na), the factor of energy resolution causing an interaction of elements (e.g., Pb and As), wrong choice of in-built calibration modes, measurement from the top surface of a layered matter in which the in-depth penetration/absorption of X-ray photons depends on their energy, etc.) [31,32] initially led to a strong suspicion of the proponents of the alternative methods [21,22,30], more precise but micro-destructive [6–9] as to the accuracy of the pXRF measurements. However, the non-invasive nature of pXRF measurements leads to an increase in the use of the technique, and the measurement procedures make it possible to largely overcome the drawbacks of the devices.

Table 1 shows that, obviously, the most common use of pXRF in Cultural Heritage studies concern natural silicates (obsidian) and objects made of silicates (pottery, glass, enamels), although the reliability of the procedure is certainly better for metal alloys (fewer elements, better homogeneity for the probed volume, etc.).

Table 1. Number of pXRF papers retrieved from the database of Web of Science® (Clarivate Analytics) published between 2002 and 2019; some representative examples can be found in Refs. [13–34].

Object	Question	Number of Studies
Obsidian and prehistoric tools	Origin, trade	85
Pottery (body)	Origin, technology	48
Glaze and enamels	Composition, technology	22
Paintings, frescoes	Colouring agents	21
Bronze	Composition	18
Rock art	Colouring agents	8
Glass beads	Origin, trade	6
Metal residues, slags	Technology	5

The importation of ceramic materials produced in China began in increasing quantities after the development of regular trade activities in the 17th century between the Far East and Europe by Portuguese traders, and then the Dutch, English, and to a lesser extent, French and Swedish East India companies [38,39]. Alongside the famous porcelains, which had monochrome or blue-and-white decorations, celadons in the view of jade, and red ceramics, called '*boccaro*' or '*bucaro*', were part of the shipments [9,40,41]. Ehrenfried Walther von Tschirnhaus and Johann Friedrich Böttger discovered a kaolin rich in iron oxide while investigating the raw materials that could lead to imitating Chinese (hard-paste) porcelains [41]. This discovery enabled them to produce, red stonewares, in the vernacular so-called, '*Jaspisporzellan*' (analogically 'marbled' porcelain), similar to those produced in Yixing, China, first in Dresden and then in Meissen [35,36,41]. Such Chinese objects were present in the collection of Augustus II, (known as Augustus the Strong, Grand Elector of Saxony, King of Poland, Grand Duke of Lithuania), and Böttger made moulds from these objects to produce real replicas [41].

From a ceramic point of view, stoneware is very close to porcelain: the proportion of the vitreous phase is similar, and, therefore, the open porosity is low, ranging from about 9% to 3% (<1% for translucent porcelain) [42–46]. On the other hand, the dissolution of quartz grains is more limited. This very good densification makes it possible to polish stoneware such as semi-precious stones [9,35], a technique known to J.F. Böttger, who was trained in lapidary techniques. The firing temperature is lower than that of porcelain (respectively, around 1150 to 1300 °C for stoneware and 1250 to 1450 °C for traditional porcelains) [44,45] which gives the stoneware good mechanical properties despite the poor development of mullite needles [44–48].

Stoneware is usually obtained by using a stoneware clay ('*argile grésante*'). The characteristics of such clays have been identified in Normandy (Beauvaisie), Burgundy (Puisaye-Forterre), the region of Provins in France, but also in Germany (Rhineland, Westerwald), England (East-Anglia, Devon and Dorset), Czechia (Cheb), Holland (Delft), etc., by potters

from at least the Middle Ages. Mineralogically, these 'clays' are made of kaolinites or halloisites (in fact, kaolinite is not a clay stricto sensu due to the absence of compensating cation in the inter-slab layer of the phyllosilicate, hence its greater refractoriness and lower plasticity) [42,43] and illites—rich in organic materials such as humic acids; they are also called 'ball clays', 'plastic clays', or 'flint clays'. Illites highly contain iron, hence the reason of the more or less pronounced red color in almost all stoneware. Note that iron oxides react in reducing atmosphere (promoted by the organic matter) with fluxing oxides (Na_2O, K_2O, CaO) to form a liquid phase at temperatures lower than 800 °C, promoting the densification but also the formation of gas bubbles. Usually, these "clays" also contain "sand" (grains of quartz).

While European stonewares produced before the 17th century exhibit specific stylistic and color/aspect characteristics sufficient to identify them without any doubt, later productions, especially from the 18th century, share a common aesthetic that could make identification more difficult. Having shown its effectiveness, in particular in distinguishing the copies of Chinese models made by Böttger, the work carried out by mobile X-ray fluorescence (pXRF) on the '*boccaro*' stonewares attributed to Meissen [32,33] was extended to objects attributed to other European production sites: England, Holland, Russia, and France.

A limited number of studies about the characterization of Böttger red stoneware have been published since the 1990s [9,35,36,49–55], particularly about the Delft and other European productions. With this study, the chemical characteristics of European (nine unglazed objects produced in England, France, Russia, and Holland) and Chinese (one enameled and 10 unglazed objects) red stonewares were defined by using an on-site characterization technique, pXRF, which allowed a methodology to be created for distinguishing the differences depending on the provenance and authenticity of the artefacts. The recent analyses were compared with the previously studied [35] 25 unglazed, polished, and non-polished objects, assigned to have been made by Böttger at Meissen, in addition to the reference materials published in the literature [54,55]. Technological differences, which depend on the provenance of the artefacts, were revealed as a result of this study.

2. Experimental

2.1. Artefacts

Figure 1 presents the analyzed objects described in detail in Table 2, belonging to the collections of the National Ceramic Museum founded by Alexandre Brongniart [56] at the beginning of the 19th century in Sèvres (now called Cité de la Céramique after merging with The National Sèvres factory founded in 1740 and established a few years after as a Royal factory). A total of 11 objects are attributed to China (Yixing), three objects to England, three to Holland, two to France, and one to Russia. The data obtained on these objects will be compared to the data obtained from 50 unglazed and 21 enamelled Böttger objects (actually including one Chinese, some fakes and modern copies), that were previously published [35,36] The reader should refer to these papers to see the objects and their characteristics. The surface of most objects is left as sintered, except two of them, which are enamelled. Additionally, four or five of them have a surface smoothed/polished to give a gloss effect. Some have the marks indicated in Table 2. The absence of enamel on the surface prevents some of the weaknesses of the portable XRF instrument because the area analyzed is homogeneous and can be considered as of infinite thickness for the X-ray excitation. Furthermore, the authorization of the instrument placement in gentle contact with the artefact allows to reduce the distance of the X-ray pathway in free air (Figure 2).

Many selected objects entered the museum's collections in the 19th century, after being collected in 1837 by exchange with Dresden Museum Collections by the Director of the Sèvres Factory, Alexandre Brongniart, to constitute a technological and historical museum which brings together the most representative objects of ceramic art of every origin. This selection, according to the criterion of pedigree in arriving in the museum's collections at the beginning of the 19th century, is an important guarantee of the representativeness for many of the objects.

Figure 1. Objects examined in this study. See Table 2 for more information (FR: France; EN: Great Britain; RU: Russia, CH: China).
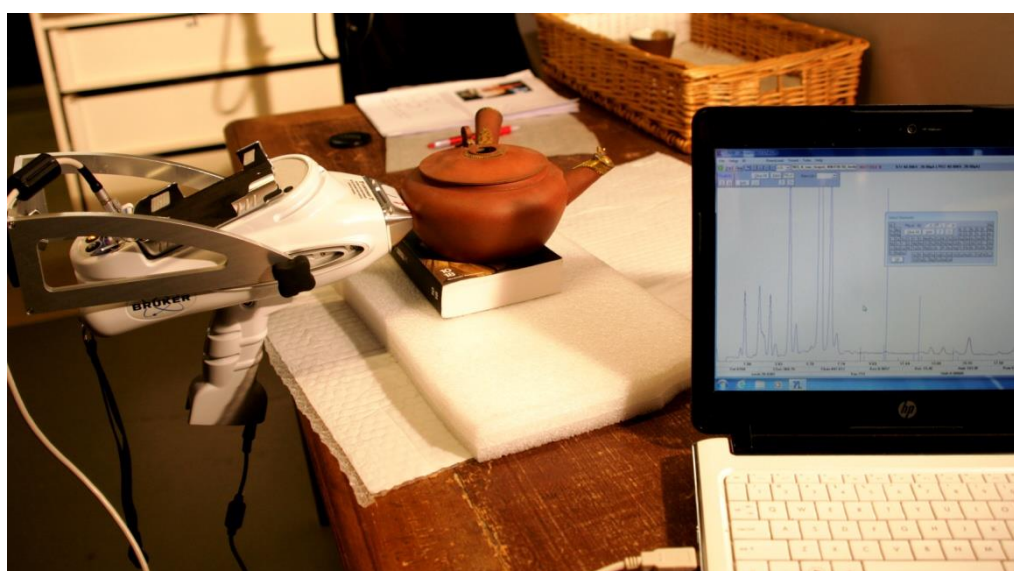

Figure 2. View of the measurement set-up. The XRF spectrum was evaluated after recording on the laptop screen.

Table 2. Description of the objects studied and presented in Figure 1.

MNC Code	Origin	Approx. Production Date	Object (Factory)	Dimension (cm)	Surface	Couleur	Remarks, Date of Entrance in the Collection
903.4		18th c.	Teapot	H:9.9; L: 18.9 × 21.5	Unpolished	Brown-red	1826 (from Salé Coll.)
10,169.908	China (Yixing)	19th c.	Teapot	H:5.6; D:6; L:8.9;	Glossy	Red	Expected to be a copy of a teapot made by Hui Mengshen, 1894 (Coll. Frandon and de Voltais)
466		18th c.	Teapot (feasan)	H:11.4; D:6.5;L:13.9	Unpolished	Brown-red	1806
434.6			Teapot	H:16.6; D:11.6; L:18.6	Unpolished	Brown-red	
457		Unknown	Teapot	H:16.6; D:11.6; L:18.6	Unpolished	Brown-red	
459		Unknown	Teapot	H:16; D:9.8; L:14.8	Unpolished	Brown-red	
7349.1		Unknown	Tea box	H:17.4; D:10;L:11.7;	Unpolished	Dark-brown	Manufactured in Hle Sing or Y-Ching, 1878
3984.3		18th or 19th c.	Teapot	H:10.9; D:6.7; L:17.2;		Dark-brown	1849
903.1		unknown	Teapot	H: 6.5; D:7.4; L:10.4;	Glossy	Dark brown	
23,578		19th c.	Teapot	H:14.8; D:12.6; L:18.2;	Enamelled decor	Many colours	1974
3985.3		Unknown	Tea cup	H:6; D:7.5 D (base):3.7	Interior enamelled in white	Dark-brown	Mark: made at Chang-ai, Kiang-nan, 1849
SC 10-169-1056 *			Teapot	H::~10	Unpolished	Light red	Assigned as Yixing
SC 462 *	Germany		Teapot	H:9.4; D~13	Unpolished	Red	Assigned to Böttger
14,820	England	19th c.	Horn-shaped vase (Isleworth)	H~20	Glossy	Red	1908 (from de Grollier Coll.)
2227.7		1836?	Candlestick (J. Wedgwood Factory)	H~12	Unpolished	Red-brown	1836 (from M. Wood Coll., Burslem)
2450.1		1837?	Decoction pot (J. Wedgwood Factory)	H:25		Red	1837 (from I. Taylor Coll.)
3589.5	France	Unknown	Burette	H~20	Glossy	Red	1846 (from M. Le Coq Coll.)
310.2		1790	Ewer	H:19.3; D:8; L:11.4;	Glossy	Red	1802
19,832	Russia	1852	Ewer (Mejigorie Factory, Kiev)	H:16	Unpolished	Brown-red	1938
467.3	Holland (Delft)	First quarter of 18th c.	Doedelrakspeler statuette (bagpiper), (Lambertus van Eenhoorn mark)	H:17; L:9;	Glossy	Red	1806 In the past assigned to a Böttger copy

Table 2. *Cont.*

MNC Code	Origin	Approx. Production Date	Object (Factory)	Dimension (cm)	Surface	Couleur	Remarks, Date of Entrance in the Collection
14,808		1680–1708	Teapot (De Grecroonde Factory- Ary de Milde mark)	H:10; L:14;	Glazed	Black	
2244.2		1680–1708	Teapot (De Grecroonde Factory- Ary de Milde mark)	H:11.5; L:17	Glossy	Brown-red	1836 (from Dresden Coll.)

* The images of these objects are shown in [35].

2.2. Portable X-ray Fluorescence (pXRF)

X-ray fluorescence spectroscopy analysis was performed using a Bruker Tracer III-V (Bruker AXS, Karlsruhe, Germany) portable system equipped with a rhodium (Rh) target X-ray tube that was operated at 40 kV, 20 μA (for high-Z elements) and 15 kV, 44 μA (for low-Z elements) to identify the network modifiers and coloring/gilding agents found on the glaze, as previously described [35,36]. A vacuum pump was used during the measurement at a lower voltage to enhance the detection of low-Z elements (from aluminum to titanium). The beam size at the surface was roughly 0.15 cm^2.

The measurements were carried out on at least three different areas of the body. The results are reported as the mean values of all of the individual point analyses done on each object. The raw data, which represent the elemental composition of the objects' bodies, are given in the Supplementary Material. For a qualitative evaluation purpose, Kα lines of Al, Si, K, Ca, transition metal elements (Ti, Cr, Mn, Fe, Cu, Zn) and trace elements (Rb, Sr, Y, Zr), as well as the L spectral lines of lead (Pb), were taken into consideration. Silicon is the major element of both glaze and body layers (Si counts are measured between 10.000 (min.) and 40.000 (max.)). In order to compare current and previous measurements, the mean area counts of most of the elements are normalized by those of Si in addition to eliminate the effect of the varied distance of the instrument tip and analysis surface.

The previous study in 2012 was only carried out on Böttger and Chinese stonewares to distinguish the technological differences of these two production centres. Thereafter, in 2013, we increased the number of production places (France, England, low countries, and Russia) but also re-analyzed two objects already studied with another series of the same XRF instrument (Bruker Tracer III-V) in order to evaluate the reliability of the procedure (measurement and/or associated data treatment) on the results.

2.3. Evaluation of the pXRF Data

Bruker Tracer III-V pXRF spectrometers do not contain built-in analytical modes (e.g., Soil, Mining, Rare Earths, etc.) like the later-generation pXRFs [31,32,57,58]. These modes operate at different voltages, e.g., for Mining mode double excitation at 15 kV and 40 kV, and for Alloy mode only one excitation at 40 kV. At the factory, these analytical built-in modes were created after performing the calibration measurements of proper standards [31,59]. The data obtained with Tracer models of Bruker were treated after recording the spectrum (Figure 3), either by interpreting the mean of area counts [35,36] or using an external calibration method. For ceramic materials, the calibration of Mud Rock, which is Mother Nature's fine grain soil, was used. Dr. Harry Rowe at the UT Bureau of Economic Geology selected those that cover an extensive range of elements (from low-Z (Na) to high-Z (Pb in our case) elements) found in natural soil and ceramic materials. The calibration files, MA1 (for major elements) and TR2 (for trace elements), were provided for each instrument by the application scientists of Bruker Company. These files were re-formulated depending

on the energy resolution of each instrument, even though they have the same model. The measurements were carried out in 2012 with a Tracer that had an energy resolution of 210 eV and the measurements in 2013 with an energy resolution of 180 eV. Since the XRF method cannot measure C, O, and H, the weight percentage of the elements does not add up to 100 percent. Instead of normalizing the elements' concentrations to 100, we normalized the data by dividing the weight percent of Si content in each measurement, silicon being present in all analyzed spots. Each color is referred to a different production center (labels in red, China; dark yellow, Böttger; grey, Delft; green, England; pink, Russia; blue, France). Through this evaluation procedure, we were able to compare both 2012's and 2013's measurements carried out with different series of the same instrument. Additionally, the results of the reference materials extracted from the literature were shown with the labels in light-yellow color in the figures of scattering plots. Stoneware has the advantage of being homogeneous for the spatial area and volume probed by the measurement. Indeed, the accelerating voltage referring to the energy of the incident radiation stimulating the emission of radiation from the sample affects which elements can be excited and measured, as well as the probed volume. In the case of the use of a target material (for example, in a Rh tube) the accelerating voltage needs to be 1.5–2 times the absorption edge energy of Rh. Rh K Lines is 23.224 keV, so a voltage range of 35–45 kV is required. For low-Z elements, the highest absorption edge energy would be 6.537 keV (Mn), which requires the use of a 13 kV accelerating voltage (Figure 3).
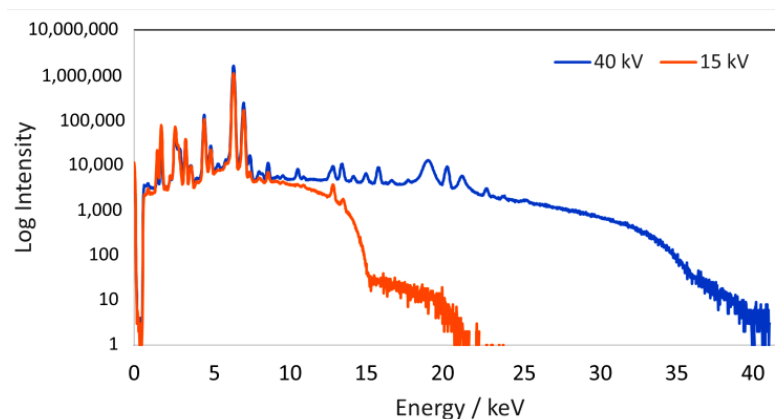

Figure 3. Comparison of pXRF spectra recorded in the same spot with 15 and 40 kV accelerating voltages (MNC 10,169.908).

The drawback will be that, for a higher accelerating voltage, a higher background will form [60]. Therefore, it is important to properly correlate the accelerating voltage and filter selection during the measurement. The sample matrix and density of the materials will also affect the detection capability. For this reason, the measurement of major, low-Z elements (Al, Si, Mg, K, Ca) is made on the top surface layer (a few microns of thickness), although the determination of heavy elements, such as Pb and Sn made up to a few hundred microns. The similarity of the composition of the artefacts allowed us to create a comparison between the objects. Moreover, the same measurement and data evalaution procedures have been applied. Statistica 13.5 (TIBCO Software Inc., Palo Alto, CA, USA) was used for drawing the scattering plots.

3. Results

3.1. Nature of Red Porcelain/Stoneware and Expected Raw Materials and Compositional Characteristics

We need first to recall which raw materials are required to produce stoneware in order to highlight the most important parameters regarding elemental composition.

According to the famous book of Brongniart [56], the paste of stoneware is produced from a 'ball clay' (e.g., a very plastic clay). Alternatively, stoneware can be prepared by mixing the China clay (2–24 wt%, rich in kaolinite or halloysite), ball clay (24–48 wt%, rich in illite), and flint (2–43 wt%, a rather pure silica stone). A small amount of marl (mixture of clay and calcareous matter) or pegmatite ('*grauen*', a mixture of quartz and feldspar/plagioclases) can also be added. By comparison, the typical composition of a porcelain paste contains 50 wt% kaolin, 25 wt% feldspar, and 25 wt% quartz. Note that 5 to 8 wt% Fe_2O_3 are required to obtain the red color. The precise composition and raw materials used by Böttger are not known, but some information has been extracted from ancient documents by Goder et al. [41]. Arcanist Johann Friedrich Böttger, in association with Ehrenfried Walther von Tschirnhaus, a famous chemist and glassmaker who designed the lenses of a solar furnace that was able to melt kaolin, searched for refractory clays in Saxony and around to prepare artefacts equivalent to imported China and developed high-temperature firing procedures. Böttger identified red refractory earths, namely 'kaolins' extracted at Okrilla, or close to Aue (Rote Sankt Andreas, Weisserden); the latter is a mixture of kaolin, quartz, mica and hematite. Furthermore, the other clays used, extracted from Zwickau, Waldenburg and Colditz in Saxony and the clay in Troschenreuth, close to Nürnberg (Bavaria), contain feldspar and/or shale. It is not established if quartz or quartzite was used. The flux used at Meissen was made of alabaster (gypsum), and/or calcite ('*spath*').

Scholars noted that the Chinese red stoneware exhibited a surface more corrugated than that of Böttger's artefacts. The optical examination of fracture or section shows that the quartz grains are actually larger in the Chinese paste in comparison with Böttger stoneware. The porosity ranges from 6% to 8%. The large amount of mullite measured in Meissen porcelain production, higher than in Chinese homologs, is related to the different composition (Meissen: ~30%wt Al_2O_3 vs. ~20%wt for Chinese porcelain [45,61]) and (expected) firing temperatures, ca. 1200–1300 °C in China, ~1450 °C at Meissen [9,41,61]. Previous pXRF analyses carried out on stonewares attributed to Böttger (Meissen factory, Saxony, Germany) production showed that the content of K versus Ca, and Ti versus Fe were very effective in distinguishing Böttger's productions from Chinese models [35,36,41]. The elements, potassium and calcium, are primarily related to the flux content, although iron and titanium are associated with the secondary phases, which color the 'earths' in red, for instance, the hematite mineral present in Okrilla and Aue rocks. Hematite, as well as brookite, are nonstoichiometric compounds with more or less important substitution of Fe atoms by Ti or Al.

3.2. Elements Associated with Fluxes

The comparison of the K_2O/Fe_2O_3, TiO_2/Fe_2O_3, MnO/Fe_2O_3, and PbO/Fe_2O_3 ratios from the compositions measured by PIXE led Swann and Nelson to identify three groups among 16 objects attributed to Böttger [53]. Our previous measurements on 71 artefacts [35,36] show two not very distant groups for the Meissen productions by Böttger and 20th century replicas of the same manufacture, while the origin of objects characterized by a lower level of iron and titanium was questioned and assigned to copy/fake. Unglazed, polished and non-polished objects were selected for the interpretation of the new results carried out on red stonewares of different production centres. In summary, previous pXRF analyses of Böttger stoneware [35,36] pointed out that rubidium and strontium, which are the natural impurities of (earth-)alkali, are also characteristic for the comparison of provenance determination in relation to the use of different fluxes containing either potassium or calcium. Figure 4 compares pXRF spectra recorded on two Delft stonewares and a Yixing

production. In most cases, compositional differences are too limited to identify visually, but in rare cases, characteristic peaks—in this case, peaks of Ca, Mn, Pb, and Rb—allow the elemental composition of different productions to be differentiated.
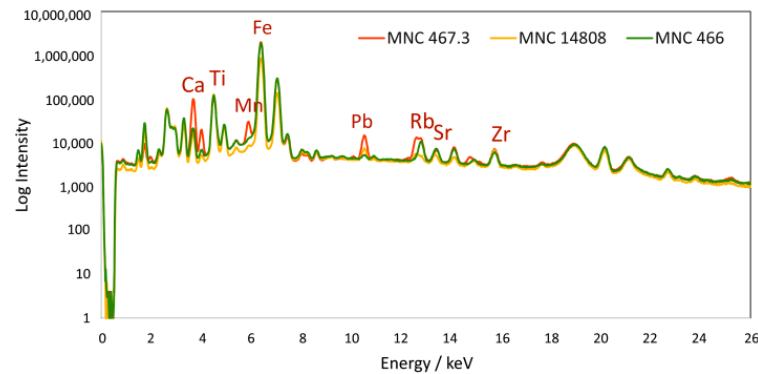

Figure 4. Comparison of pXRF spectra recorded under 40 kV accelerating voltage on MNC 467.3 (bagpiper, Lambertus van Eenhoorn mark, Delft), MNC 14,808 (teapot, Ary de Milde mark, Delft) and MNC 466 (teapot, Yixing, China) artefacts. Binary scatter plots of K versus Ca (Figure 5), normalized by Si, explicitly show the discrepancy of Delft productions from the other red stonewares produced in China and Europe. Moreover, the ewer inv. MNC 310.2 assigned to France has a similar amount of potassium (K/Si: ~0.2) in comparison with the teapot of Ary de Milde, Delft (MNC 2244.2). The minimum amount of potassium (K/Si: ~0.04) and a small amount of calcium (Ca/Si: ~0.08–0.10) are evidenced in Wedgwood productions.
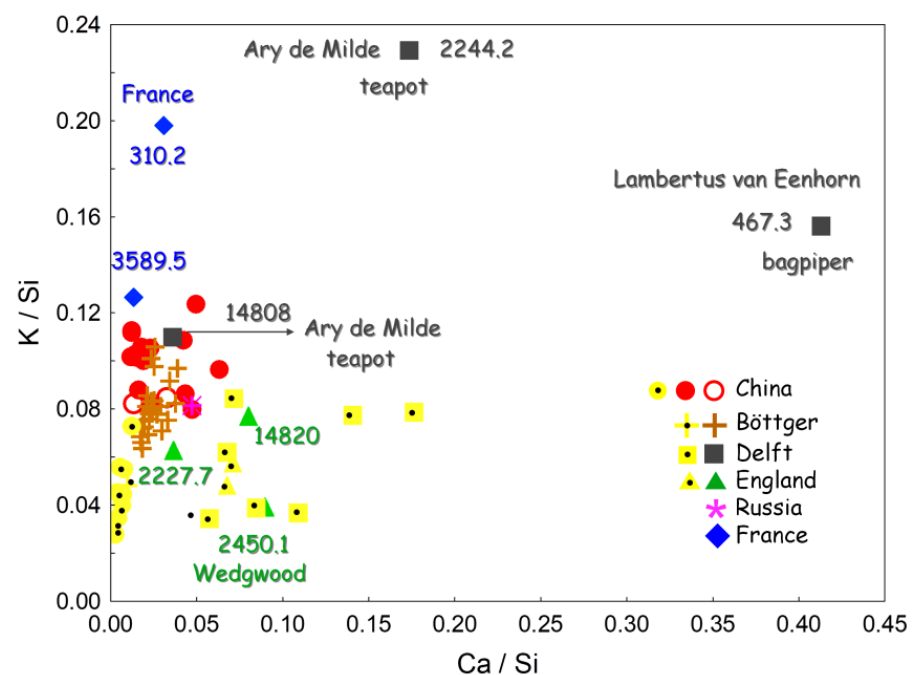

Figure 5. Scatter plots of the old (plus sign attributed to Böttger analyses carried out in 2012 and blank circle to the Chinese ones) and new data (solid circle: China, square: Delft, triangle: England, radial: Russia, and rhomboid: France) compared to the reference data (labels in yellow color) [51,52] regarding fluxing elements (K versus Ca normalized by Si) found in the composition of red stoneware.

The binary and ternary scatter plots (shown in Figures 5–7) confirm the comparability of the previous (2012) and later (2013) measurements after evaluating the data according to the Mud Rock calibration criteria. A comparison of the data collected on the Böttger *'Jaspisporzellan'* with those obtained on the other European productions shows the very

low dispersion of the element content for Meissen production; the K content is constant (K/Si ~0.3 + −0.1), although for European red stoneware the K/Si ratio varies between ~0.2 and 1.2. The Ca/Si ratio is more scattered (~0.07 to 0.25) but remains much smaller than other European artefacts (0.1 to 0.8). However, The K/Ca ratio does not make it possible to differentiate Meissen stonewares from English stonewares—note the artefact with the Ary de Milde mark shows a Ca/Si ratio of ~0.4.
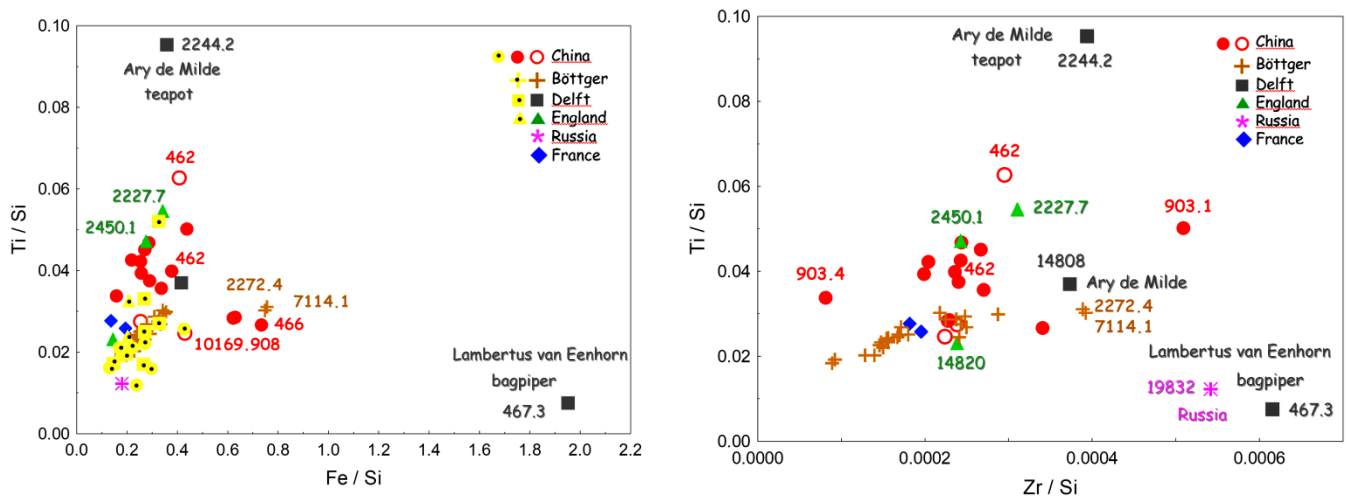

Figure 6. Comparison of the old (plus sign attributed to Böttger analyses carried out in 2012 and blank circle to the Chinese ones), new, and reference data regarding Ti, Fe, and Zr content measured on European and Chinese red stonewares compared with Meissen Böttger. See the caption of Figure 3 for the symbols.
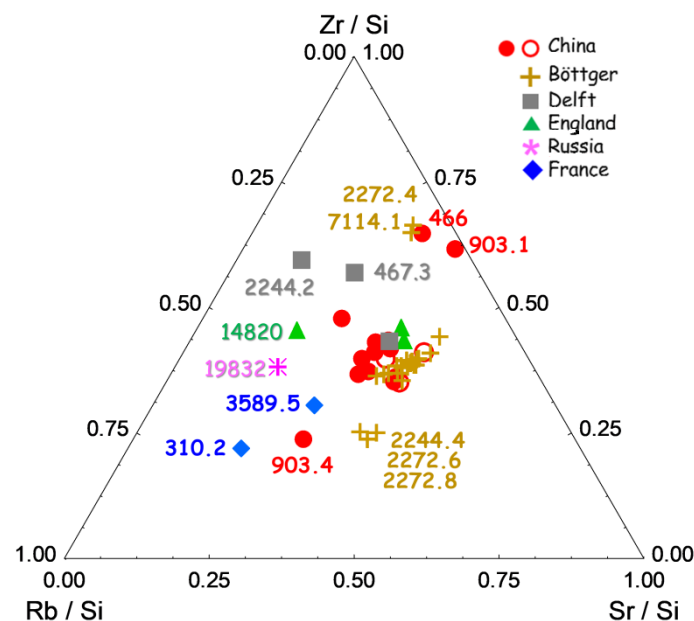

Figure 7. Ternary diagram of trace elements (Zr, Rb, and Sr) distribution in the body composition.

The main difference among Böttger productions has arisen from the distribution of trace elements (Rb and Sr) in their body composition. This distinction was previously evidenced in the first study of Böttger characterization [35]. The two Sevres objects (MNC 2272-4 and MNC 7114-1) were assigned as a Böttger production in the old museum inventory, but have been re-assigned stylistically to Chinese production by the curators [35]. This stylistic attribution was confirmed by pXRF analyses, which showed a similarity in

the chemical composition of a series of Chinese stoneware. The relatively close similarity between Meissen, Yixing, and most of the Delft productions for the major fluxing elements can be related to the selection of clays with rather similar ceramic properties (plasticity, iron and flux content, and sinterability) required for a firing in a similar temperature range and, hence, their relatively similar composition.

3.3. Elements Associated with Stable Minerals

Hematite, anatase, and rutile are commonly identified by Raman spectroscopical studies of porcelains. However, these minerals, already present in many raw materials [35,36], are sufficiently stable to not be (completely) dissolved during firing cycles. Zircon is also a minor phase of many raw materials (quartz, pegmatite, etc.) and does not react during firing cycles. Taking into account the ratio of Ti versus Fe, normalized by Si, also demonstrates the homogeneity of Böttger's data (Figure 6), except for two objects: MNC 2272-4 and MNC 7114-1. These two objects, the vases, were assumed to be Böttger productions, but the chemical composition of the body corresponds more to a Chinese production. Figure 6 also demonstrates the similarity of these objects to a Chinese artefact, MNC 466 (Table 1), attributed to the Yixing production. The other artefacts of Böttger and some of Chinese objects form a second group which have lower amounts of Fe by revealing a technological relationship. However, when the data are more focused on these two productions by discarding European red stonewares, the ratio identifies in distinguishing Meissen artefacts from Chinese stonewares, as well as from modern copies or fakes [35,36]. Ti/Si vs. Fe/Si biplot clearly identifies the Delft productions other than Ary de Milde artefacts. However, modern Russian (Kiev) artefacts exhibit low Fe content. Unfortunately, the distribution of data on English and Chinese productions overlaps.

3.4. Most Pertinent Element for the Differentiation of the Provenance

Comparison of Böttger and Chinese artefacts pointed out that Rb/Si and Sr/Si ratios, and also Zr content (Figure 7), are the most effective characteristic to discriminate the artefacts, as previously noted for the differentiation of genuine and fake Meissen artefacts [35,36]. The Zr/Si–Rb/Si–Sr/Si-plotted ternary diagram clearly distinguishes the productions among Russia, France, and Delft (Ary de Milde and Lambertus van Eenhoorn).

The main group of Chinese artefacts, which was assigned to the productions of Yixing factories, is clustered within the group of Böttger and Chinese artefacts previously studied in 2012. Exceptionally, a series of Chinese (MNC 466, MNC 903.1) and Böttger (MNC 2272.4, MNC 7114.1) objects are observed with the higher amount of Zr and lower amount of Sr and Rb. However, the Chinese teapot, MNC 903.4, is located separately from the other Chinese artefacts because it contains a very low amount of Sr and Zr. The few artefacts produced in Russia are rich in trace elements Rb, Sr, and Zr. The bagpiper with a Lambertus van Eenhoorn mark and the glossy teapot with an Ary de Milde mark, produced in the factory of De Grecroonde (Delft), differentiate materially from the main group, and especially from the other glazed teapot which is assumed to be produced in the same factory, by Ary de Milde also, according to the content of trace elements. The chemical differences in the raw materials used in the body of French and Russian productions also reveal the discrepancy of the provenance (i.e., raw materials) of the objects.

4. Discussion

On-site measurements clearly show the technological differences of Delft productions from the other European and Chinese productions because they are richer in both Ca and K as fluxes, which allow them to be fired at lower temperatures and, thus, at lower costs. Therefore, the use of these fluxes led to a high level of commercial success to be achieved). Moreover, they also show a discrepancy where the variation of the body composition is largely varied. Indeed, at the end of the 17th and beginning of the 18th centuries, three Dutch potters, Lambertus Cleffius, the owner of the Metal Pot, Lambertus van Eenhoorn, and Ary de Milde, were working to produce red stoneware. However, the use of different

raw materials in the same region was not expected until the chemical compositions were identified with pXRF. Additionally, the detection of trace elements reveals the importance of more precise measurements, since the literature only shows the results of major elements, such as Fe, Ti, Ca, and K [54,55], which cannot distinguish provenance differences. In addition to Dutch productions, Wedgwood artefacts reflect a change in the content of the body, which may reflect a transition from old (earlier-19th century) to recent (later-19th century) productions by diminishing the amount of potassium. The same case may be valid for French artefacts, depending on either the production period or the factory. It should be interesting to relate these evolutions of the technologies with increasing mass production and economic constraints.

The analyses observed the influence of Chinese red stoneware technology's impact on European ceramic makers in the 18th and 19th centuries. Most of them were influenced aesthetically, but Böttger used not only the same style but also rather similar technology by mixing similar raw materials.

5. Conclusions

The calibration and normalization procedures demonstrated the validity of old and recent analyses were carried out with the same model but a different series of pXRF instrument. The interpretation of the data is as essential as the measurement process. Additionally, the analyses carried out with our pXRF instrument were comparable with the old measurements carried out at the laboratory with highly sensitive instruments (e.g., ion beam techniques, energy dispersive fluorescence system). Lastly, the detection of trace elements (Rb, Sr, Zr) was achievable using an on-site, non-invasive technique. This study aimed to identify the differences regarding the raw materials used by different potters who worked in different countries (Russia, Holland, England, France, Germany, and China) in the 18th and 19th centuries. The analyses showed that Böttger was influenced directly by the technology of Chinese productions and used a similar recipe for making red stoneware. However, Delft productions differ locally and internationally from the other factories in terms of flux selections rich in calcium and/or potassium, and these characteristics could have been a determining factor for the low production costs and the success of these productions.

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