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Retrospective Study of the Feasibility of Using EDXRF for the Attribution of Blue and White Porcelains

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Two important aspects of the feasibility of using EDXRF for the attribution of porcelains were solved. First, elements such as Mn and Co were defined, and identified as elments characteristic of the colorant, so ratios between their concentrations (e.g. Mn/Co) are meaningful parameters. Second, it was found that elements characteristic of the colorant diffuse from the colorant into the glaze layer during high-temperature firing. Therefore, the glaze layer also contains information on the colorant which can be revealed by EDXRF. It was also shown that the half-value thicknesses calculated for Rb, Sr, Y and Zr coming from the body of the porcelain can contribute to the EDXRF results. Therefore, the EDXRF results contain information from the glaze, colorant and the body. This confirms the feasibility of the attribution of porcelains using EDXRF, which is based on the variation of the materials used for the glaze, colorant and body in different periods and localities.

INTRODUCTION

In recent years, much research has been carried out on the attribution of Chinese porcelains using non-destructive energy-dispersive x-ray fluorescence (EDXRF) spectrometry. The criteria used for the attribution include the Mn/Co ratio,[1] the relative intensities of the K lines of Rb, Sr, Zr and Nb[2] and the Zn Kα/Rb Kβ ratios.[3] This research has provided very useful and convenient methods for solving the problem of the attribution of Chinese porcelains.

The present paper is devoted to a retrospective study of the feasibility of using EDXRF for the attribution of porcelains. There are two main questions we have to answer. First, we need to know the ratios between elements and why these are meaningful and required. It will be shown that the elements characteristic of the colorant (such as Mn and Co) will vary according to the density of the blue picture, and ratios between these characteristic elements of the colorant (e.g. Mn/Co) are unique for a piece of porcelain and are thus meaningful. The second question immediately arises as it is well known that, in an EDXRF analysis, only a very thin layer at the sample surface will contribute to fluorescent x-rays. Therefore, the concentrations of the elements Mn, Fe, Co, Ni, Ti, Cu, Zn, Ga, Pb, As, Sr, Y, Zr, Ba and La measured in blue and white porcelains should reflect those in the glaze layer, although calculations of half-value thicknesses show that some elements in the body of the porcelain also make contributions. The question is why we can used information on elements such as Mn and Co for the attribution even when they are known to be characteristic of the colorant.

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ELEMENTS CHARACTERISTIC OF THE COLORANT

To answer the first question, we will first have to define and identify the elements characteristic of the colorant. The method is based on the examination of typical EDXRF spectra for porcelains from different periods. The EDXRF system employed for the present research was a Philips DX-95 EDAX. The target was molybdenum and the target angle was 45°. The maximum tube voltage was 50 kV and the current was 500 μA. The resolution, defined as the full width at half maximum of the Mn Kα line, was 164.2 eV. Regarding the samples investigated in the present research, Jingdezhen blue and white porcelains of the Ming and Qing dynasties were supplied by the Palace Museum, Beijing, China, and modern Jingdezhen blue and white porcelains were purchased from the market in Hong Kong. Figures 1 and 2 show typical XRF spectra of the antique and modern porcelains, respectively.

From Figs 1 and 2, it can be seen that Mn, Co and Ni come mainly from the colorant. There are substantial amounts of Fe recorded for the areas with the colorant in addition to those without the colorant. The

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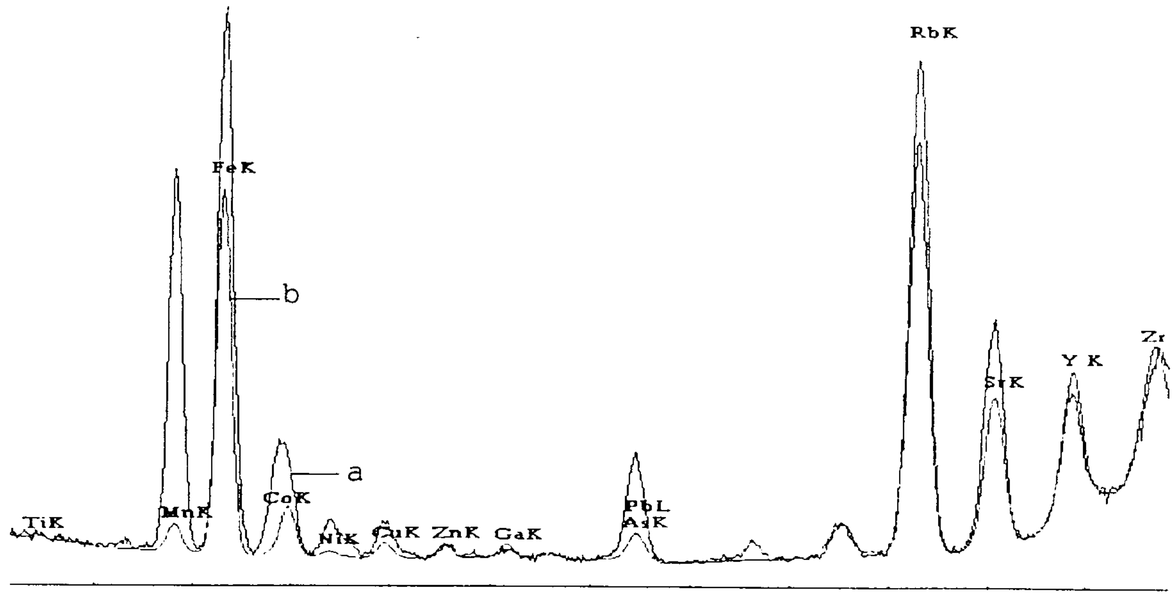

Figure 1. XRF spectra of a blue and white porcelain of the Hongzhi period (mid-Ming dynasty). (a) From an area including the glaze, colorant and the body; (b) from an area including only the glaze and the body.

elements As and Cu show similar behavior in some porcelains, e.g. the behavior of As as shown in Fig. 1. These elements are defined to be the characteristic elements of the blue colorant. The abundance of the elements is a variable which changes with the density of colors on the porcelains. Hence absolute values for their concentrations are not meaningful. Instead, our experimental results show that ratios between their concentrations are unique for a piece of porcelain. Therefore, these ratios have objective and practical values, and are required for meaningful analyses. On the other hand, the ratios between elements which are and are not characteristic of colorants are also variable and cannot be used for the identification of the attribution or origin of the porcelain.

DETECTABILITY OF ELEMENTS CHARACTERISTIC OF THE COLORANT

Half-value thickness

As mentioned in the Introduction, it is well known that EDXRF analysis mainly gives results for a very thin layer at the sample surface. When a fluorescent x-ray passes through a thickness equal to the half-value thickness, its intensity will decrease to half its original value. According to the Lambert law, the half-value thickness, $t_{1/2}$, for different elements in the porcelain samples can be calculated as follows. The intensity I recorded for an

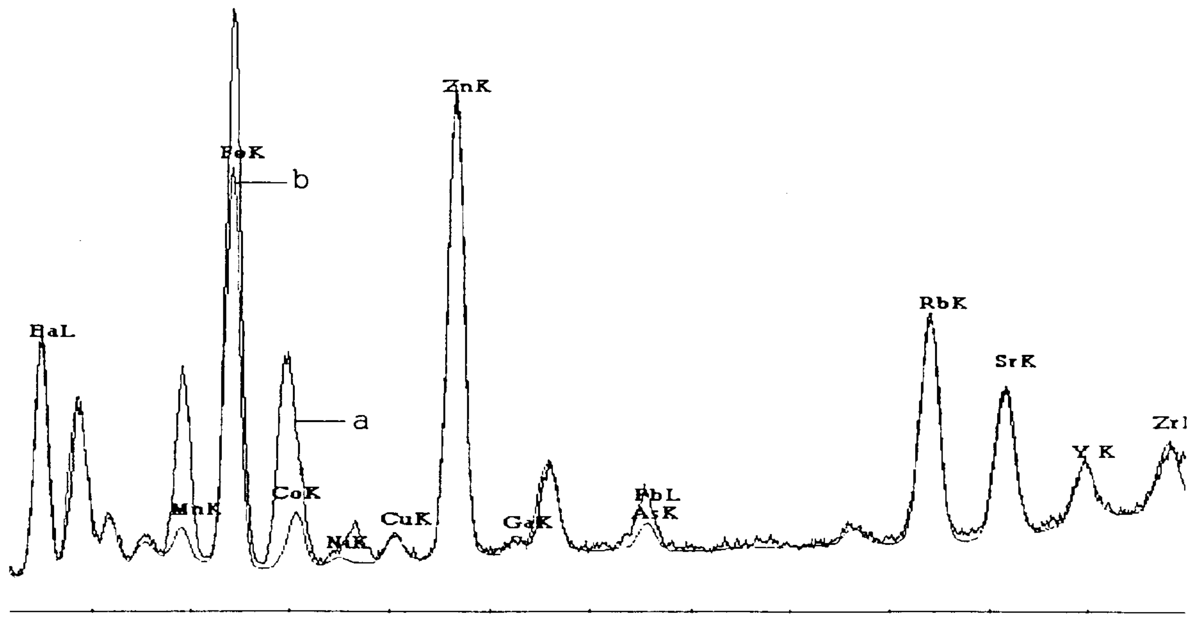

Figure 2. XRF spectra of a modern blue and white porcelain. (a) From an area including the glaze, colorant and the body; (b) from an area including only the glaze and the body.

Table 1. Half-value thicknesses of elements in blue and white porcelains

Atomic number	Element	Analytical line	Half-value thickness (μm)
12	Mg	Kα	1.1
13	Al	Kα	1.8
14	Si	Kα	2.3
15	P	Kα	1.3
19	K	Kα	5.8
20	Ca	Kα	6.5
22	Ti	Kα	9.3
23	V	Kα	12.7
24	Cr	Kα	15.9
25	Mn	Kα	20.8
26	Fe	Kα	25.9
27	Co	Kα	31
28	Ni	Kα	36
29	Cu	Kα	45
30	Zn	Kα	54.4
31	Ga	Kα	66.6
33	As	Kα	95.2
37	Rb	Kα	183
38	Sr	Kα	217.4
39	Y	Kα	284
40	Zr	Kα	309
56	Ba	Lα	9.1
82	Pb	Lα	95.5

analytical line with an original intensity I_0 at a depth t (cm) from the sample surface is given by

$$I = I_0 \exp(-\mu_{mz} \rho t) \tag{1}$$

where ρ (in g cm^{-3}) is the density of the sample, μ_{mz} (in cm^2 g^{-1}) is the total mass absorption coefficient for the element with atomic number Z contributed by 11 essential oxides in the porcelain samples, i.e.

$$\mu_{mz} = \mu_{z1} w_1 + \mu_{z2} w_2 + \mu_{z3} w_3 + \cdots = \sum_{i=1}^{11} \mu_{zi} w_i \tag{2}$$

where μ_{zi} is the mass absorption coefficient for the element with atomic number Z contributed by the ith oxide and w_i is the concentration percentage of the ith oxide in the sample. The 11 oxides, namely, SiO_2, Al_2O_3, TiO_2, CaO, Fe_2O_3, MgO, CoO, K_2O, Na_2O, P_2O_5 and MnO_2, are taken as the basic components of the glaze layer of the blue and white porcelains. Their average contents in the glaze layer and the blue colorant in porcelains of the Yuan, Ming and Qing dynasties were determined according to Ref. 4, and are 69.61, 14.70, 0.15, 5.38, 1.03, 0.26, 0.31, 2.60, 1.96, 0.18 and 1.62% respectively, summing to 97.8%.

The average density of porcelains was determined experimentally. Sixteen pieces of broken porcelain of the Ming and Qing dynasties were employed for this purpose. Circular discs with a diameter of 4 cm were cut from these pieces on areas with small curvature. The volume was measured using a vernier micrometer and the mass was measured using an electronic–optical analytical balance. The average density for porcelains was determined to be 2.337 g cm^{-3}. From Eqn (1), the half-value thickness can be expressed as

$$t_{1/2} = \frac{0.693 \sin 45^\circ}{\mu_m \rho} \tag{3}$$

where we have put $I = 0.5 I_0$ and the emergent angle of the fluorescent x-ray photons to reach the detector is 45°. Using Eqn (3), the half-value thickness for 23 elements, namely Mg, Al, Si, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Ba and Pb, which are likely to be involved in the EDXRF analysis of porcelains, were calculated and are given in Table 1.

Table 2. Concentrations (ppm) of various elements analyzed for two types of samples using ICP-AES and NAA: (A) including the glaze, colorant and the body and (B) including only the glaze and the body

Porcelain	Type	Mn	Co	Ni	As	Method
Hongzhi						
(mid-Ming dynasty)	A	6406	886	157	—	ICP-AES
	B	525	6	10	—	ICP-AES
	A	—	1030	—	141	NAA
	B	—	9	—	0	NAA
Jiajing						
(late Ming dynasty)	A	1992	1028	30	—	ICP-AES
	B	352	2	6	—	ICP-AES
	A	—	1120	—	24	NAA
	B	—	3	—	2	NAA
Kangxi						
(Qing dynasty)	A	4732	995	70	—	ICP-AES
	B	504	1	7	—	ICP-AES
	A	—	1130	—	35	NAA
	B	—	1	—	2	NAA
Yongzheng						
(Qing dynasty)	A	7898	1782	35	—	ICP-AES
	B	686	2	6	—	ICP-AES
	A	—	2060	—	11	NAA
	B	—	3	—	1	NAA

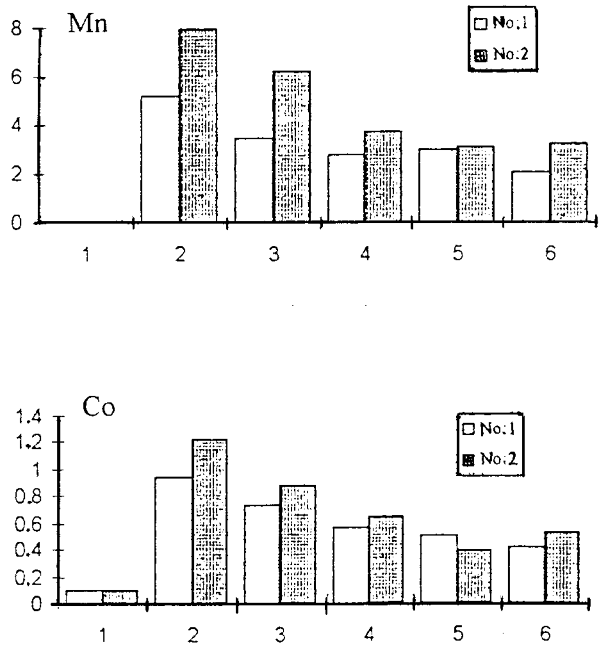

Figure 3. Distribution of Mn and Co in the glaze and the colorant of the porcelains. No. 1, blue and white porcelains of the Qianlong period (Qing dynasty); No. 2, blue and white porcelains of the Chenghua and Hongzhi periods (Ming dynasty). The ordinate is the relative concentration and the abscissa represents the layers of glaze and colorant. 1, Surface glaze layer; 2, blue colorant; 3–6, four layers from the colorant to the surface glaze layer with equal thickness, which is about 68 μm for sample 1 and 99 μm for sample 2.

As mentioned before, the intensity of a fluorescent x-ray will decrease by half when it traverses one half-value thickness, so effectively the x-ray cannot penetrate a critical thickness defined by 6–7 half-value thicknesses for detection. Blue and white porcelains are underglazed colored porcelains. Both a previous investigation[4] and the present study showed that the thickness of the glaze layer is in general 200–500 μm. From Table 1, it is seen that the EDXRF results are mainly contributed from the glaze layer, except for the elements Rb, Sr, Y and Zr.

Experimental findings

To answer the question of why we can use information on elements such as Mn and Co for the attribution even when they are known to be characteristic of the colorant, two methods were employed to reveal the behavior of these elements in the glaze and the colorant. The first method is based on inductively coupled plasma atomic emission spectrometric (ICP-AES) and nuclear activation analysis (NAA) methods. The ICP-AES analyses were carried out at the National Research Center of Geoanalysis and the NAA analyses at the Atomic Science Research Institute of China. Layers with a thickness of 1 mm were sliced off the surface of the porcelain sample and separated into two types: (A) those including the glaze, colorant and the body and (B) those including only the glaze and the body. These were then ball-milled and homogenized. The results of the analyses are given in Table 2. These results show that (1) the abundances of Mn and Co differ drastically for areas with and without color, and this further supports our EDXRF results above and the conclusion that these are elements characteristic of the colorant; and (2) some of these characteristic elements have somehow diffused from the colorant into the glaze layer during the high-temperature firing process.

The second method is based on electron probe microanalysis (EPMA). The EPMA analyses were carried out at the Institute of Mineral Deposits of China. The surface glaze layer, colorant and four layers from the colorant to the surface glaze layer with equal thickness were analyzed using EPMA. The results are illustrated in Fig. 3, which show that there are no abrupt changes in the composition between the colorant and the glaze; instead, there are gradients of element concentrations resulting from the diffusion of colorant elements into the glaze layer during the firing. Therefore, the glaze layer also contains information on the colorant.

CONCLUSIONS

We have answered two important questions on the feasibility of using EDXRF for the attribution of porcelains. First, we have defined and identified elements such as Mn and Co as elements characteristic of the colorant. Therefore, absolute values for their concentrations are not very meaningful. Instead, ratios between their concentrations (e.g. Mn/Co) are unique for a piece of porcelain and are required for meaningful analyses. For example, the Mn/Co ratios for samples 1 and 2 in Fig. 3 are about 5.2 and 6.7, respectively. On the other hand, the ratios between elements which are and are not characteristic of colorants are also variable and cannot be used for the identification of the attribution or origin of the porcelain. Second, we have found that elements characteristic of the colorant diffuse from the colorant into the glaze layer during the high-temperature firing. Therefore, the glaze layer also contains information on the colorant.

It has also been shown that the half-value thickness calculated for Rb, Sr, Y and Zr coming from the body of the porcelain contribute to the EDXRF results. From the above, it is seen that the EDXRF results contain information from the glaze, colorant and the body. This confirms the feasibility of the attribution of porcelains using EDXRF, which is based on the variation of the materials used for the glaze, colorant and body in different periods and localities.

During the study, we also confirmed a signature for modern porcelains. When the XRF spectrum of a modern Jingdezhen blue and white colorant (Fig. 2) is compared with that of a Jingdezhen blue and white colorant of the Hongzhi period (Fig. 1), the former shows much more prominent Zn Kα and Ba Lα peaks. Some previous studies have adopted these two peaks as signatures of modern porcelains.[3,5] According to the half-value thickness calculated for these two elements, they should come from the glaze and/or the colorant. The results shown in Fig. 2 indicate that they are not characteristic elements of the colorant.

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