Article

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Determination of Composition of Raw Materials for Porcelain Fabrication by XRF, TOF-SIMS, and XPS Methods for Further Porcelain Art Items Characterisation and Detection of Modern Counterfeits

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Abstract: Modern surface analysis techniques are expanding significantly possibilities in description and attribution of historical artefacts. The present study is aimed to compare analytical ability of the X-ray fluorescent analysis (XRF) typically applied for studies ceramic art items with novel surface analysis methods: time-of-flight secondary ions mass spectroscopy (SIMS) and X-ray photoelectron spectroscopy (XPS) that were applied on measurements of elemental compositions of powder raw materials for porcelain fabrication: pegmatite P-1, Vesco-prima clay, kaolin, bone earth, dolomite, and feldspar. It was shown that SIMS successfully measures light elements unnoticeable for XRF such as lithium, beryllium, boron and heavy impurities not found out by XRF such as cobalt, cerium, copper, rubidium, vanadium. XPS has found thorium in the kaolin sample that was not detected by SIMS and XRF. The paper provides also values of chemical shifts of some XPS lines observed in materials under examination. The obtained information on relations of basic and impurity elements revealed by XRF and SIMS together with XPS chemical shifts data could be used to expose contemporary falsifications of historical porcelain and to attribute porcelain items during conservation process.

Keywords: X-ray fluorescent analysis (XRF); secondary ions mass spectroscopy (SIMS); X-ray photoelectron spectroscopy (XPS); porcelain; pegmatite; Vesco-prima clay; kaolin; bone earth; dolomite; feldspar

1. Introduction

Application of analytical chemistry methods to describe porcelains composition was started dynamically in the second half of the 19th century. So the monograph [1] presents chemical compositions of porcelain mixtures used in the Imperial Porcelain Manufacture at different historical periods from its establishing to the beginning of the 20th century. Also the book [2],(pp. 28 – 29) gives compositions of porcelains fabricated on various factories in France, Saxony, Bohemia, China, and Japan. But the key disadvantage of the solution chemistry is the need to dissolve objects under study so this approach seems to be inapplicable for art history expertise of historical and contemporary ceramic art items.

Development of physical methods for non-destructive analysis of structure and composition of solids such as fluoroscopy, X-ray diffraction, X-ray fluorescent analysis, etc. have become widely used in materials science including characterisation historical objects (archaeometry) [3] and attribution art history items. X-ray fluorescent analysis (XRF) is estimated now as a commonly used method for such tasks [4] including determination compositions of historical ceramic art items [5].

In last decades in addition to the above mentioned methods the new ones such as X-ray photoelectron spectroscopy (XPS), Auger electrons spectroscopy (AES) and secondary ions mass spectroscopy (SIMS) with high spatial and depth resolution are are starting to applyin archaeometric tasks for better identification of materials and understanding technologies and mastership of artefacts fabrication [6]. So SIMS was applied for investigation of historical tapestries [7] and parchments [8]. Recently, various research teams in the world [9–12] have demonstrated the advantages of complex studies of historical artefacts using sets of modern physical methods including ones using synchrotron sources [11].

So this research was aimed on the comparative estimation of analytical possibilities of the XRF as a commonly used technique with SIMS and XPS methods for ceramic art items studies: SIMS can detect elements in trace concentrations while XPS is able to resolve multiple oxidation degrees of elements. The powder samples of raw components for porcelain fabrication were selected as most favourable for XRF because their uniform composition eliminates typical XRF problem with difference in secondary X-rays emission depth for various elements that makes some difficulties in analysis of sintered ceramics especially with glaze and painting layers.

AES was also tested on these samples in the frame scanning mode to get analysis area comparable with SIMS and XPS but it did not demonstrate any preferences comparing to XPS in this case: AES sensitivity was about 0.2 %at., and its main advantage: the focused electron beam with high locality examination — was not useful in this case of homogeneous powder samples. So these results were not included in this paper. From other hand, AES could be very useful in studies such non-homogeneous objects as sintered ceramics [13] including painting layers [14] where various components of the ceramic mass and pigments differ by their composition.

2. Materials and Methods

There were selected following powder samples of raw materials for porcelain fabrication used currently in Joint Stock Co. “Imperial Porcelain Manufactory” (St.-Petersburg, Russia): pegmatite P-1, Vesco-prima clay, kaolin, bone earth, dolomite, and feldspar.

The generalised elemental composition of the powders was measured by XRF using X-ray fluorescence spectrometer AXIOSmax Advanced (PANalytical, Almelo, Netherlands).

Surface composition with high depth locality were performed by SIMS method on the time-of-flight mass spectrometer TOF.SIMS5-100 (IONTOF GmbH, Münster, Germany) equipped by Bi scanning ions source with spatial resolution 25 nm and Cs and O ions sources for depth profiling. This device has very high sensitivity and mass resolution: according to information placed on the IONTOF GmbH website [15] the sensitivity is in the ppm/ppb range and mass resolution M/dM = 30 000. The data on the powder samples compositions were obtained by the averaging of several spectra obtained from the squares 500x500 μm. The elements concentrations calculations were based on peaks intensities of singly charged positive ions as:

$$C_i = \left(\frac{I_i}{\sum_{j=1}^{n} I_j}\right) * 100\%, \qquad (1)$$

where I_j is the intensity of corresponding ions peak. When an element had several natural stable isotopes its intensity was taken as a sum of isotopes intensities.

Binding energies of elements were determined by XPS on ESCALAB Mk2 (VG, East Grinstead, UK) at a vacuum of 3×10^{-8} Pa. XPS measurements were fulfilled using an X-ray Al—Mg twin anode source in Al Kα primary radiation (hν = 1486.6 eV, Au 4f3/2–5/2 full width at half maximum (FWHM) = 0.9 eV, analysed region was a circle with diameter of 10 mm). The powders were placed on the special sample holder using a conducting carbon ribbon.

The charging of dielectric samples was neutralised by the low energy electrons beam with energy of 70 eV. No charge-discharge shifts of XPS lines on the spectra were observed during spectra acquisition.

The fine structure of XPS lines was analyzed using the UNIFIT2007 [16] software. Identification of XPS lines and determination of chemical shifts values was based on XRF and SIMS results and information from NIST XPS database [17] Prior to the studies the energy scale of the spectrometer was checked using Ag reference sample.

3. Results and discussion

3.1. Comparison of XRF and SIMS analytical capabilities

The XRF results on the substances compositions are presented in Table 1. In accordance with the traditions of analytical chemistry compositions of complex oxide systems such as ores, ceramics and so on is listed for most elements in terms of oxides where oxides of polyvalent metals are given in maximal oxidation degrees. So, XRF data for vanadium compounds in slags was given for V_2O_5 oxide while XPS has demonstrated that it was presented only in V^{2+} and V^{3+} states [18]. One can see from Table 1 that XRF is enough sensitive to detect small impurities with content down to 0.003 %mass.

One can see the elemental composition of these substances determined by SIMS in Table 2. The columns of elements not detected by XRF or found in more samples than by XRF are marked yellow. Apart from lithium, beryllium and boron not detected by XRF due to physical limitation we found impurities absent in Table 1: cobalt in practically all samples except pegmatite and dolomite in amounts from 0.0007 %at. to 0.05 %at.; cerium in kaolin (0.00085 %at.) and bone earth (0.0021 %at.); copper detected by XRF only in the Vesco-prima clay was found in comparable quantities also in the samples of feldspar, kaolin, dolomite, and bone earth; rubidium was presented in all samples excluding bone earth in amounts of a few hundredths of percent; vanadium was in all samples with the exception of pegmatite and bone earth.

Table 1. Composition of raw materials for porcelain determined by XRF, % mass.

Substance	Al_2O_3	BaO	CaO	Cl	Cr_2O_3	CuO	Fe_2O_3	Ga_2O_3	K_2O	MgO	MnO	Na_2O	Nb_2O_5
Feldspar	16.151	0.161	1.068	0.072	0.109		0.398		15.695	0.123		2.491	
Pegmatite	14.485	0.092	0.797	0.047	0.071		0.604	0.005	5.992	0.201	0.015	3.943	
Clay	30.12	0.031	0.397	0.042	0.039	0.007	0.828	0.009	1.89	0.574		0.472	0.005
Kaolin	37.466	0.016	0.253	0.038	0.016		0.531	0.009	0.465	0.297		0.182	
Dolomite	0.475		31.274	0.049			0.134		0.08	21.312		0.107	
Bone earth	0.501	0.472	53.729	0.04	0.045		0.145		0.103	1.605		0.909	

Table 1. Continued.

Substance	NiO	P_2O_5	PbO	Rb_2O	S	SiO_2	SrO	TiO_2	V_2O_5	Y_2O3	ZnO	ZrO_2
Feldspar	0.018	0.203	0.016	0.098	0.096	62.344	0.024	0.1	0.12	0.002		
Pegmatite		0.049	0.005	0.015	0.043	72.788	0.021	0.025			0.003	
Clay	0.009	0.109	0.012	0.014	0.131	52.644	0.017	1.225		0.005	0.003	0.035
Kaolin		0.187			0.072	44.384	0.003	0.546				0.015
Dolomite		0.101			0.042	1.019	0.007					
Bone earth	0.019	37.463			0.115	2.016	0.022	0.09			0.036	

Table 2. Composition of raw materials for porcelain determined by SIMS, % at. The elements not detected by XRF or detected with strong discordance between XRF and SIMS are marked yellow.

Substance	Al	Ba	Ca	Cl	Co	Cr	Cu	Fe	Ga	K	Mg	Mn
Feldspar	14.30	0.032	7.464	0.000467	**0.002939**	1.058	**0.019**	4.902	0	30.69	1.469	0
Pegmatite	28.14	0.130	2.139	0	**0**	0.034	**0**	0.893	0.025	25.85	1.010	0.056
Clay	50.40	0.033	2.822	0.000437	**0.050032**	0.050	**0.019**	0.652	0.015	19.59	1.590	0
Kaolin	70.53	0.016	3.091	0.000499	**0.001061**	0.044	**0.012**	0.705	0.011	5.041	1.164	0
Dolomite	7.80	0.090	6.345	0.000687	**0**	0.240	**0.011**	1.491	0	10.71	63.049	0
Bone earth	1.95	0.365	63.70591	7.02E-05	**0.000707**	0.104	**0.012**	0.520	0	3.90	3.390	0

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Table 2. Continued.

Substance	**Na**	**Ni**	**P**	**Pb**	**Rb**	**S**	**Si**	**Sr**	**Ti**	**V**	**Y**
Feldspar	31.20	0.0403	0.0118	0.003511	**0.0733**	0.00104	6.671	0.0144	0.159944	**1.6385**	0.0019
Pegmatite	12.58	0	0	0.00135	**0.0339**	0	28.941	0.0459	0.025852	**0**	0
Clay	7.85	0.0095	0.0021	0.002662	**0.0566**	0.00067	16.267	0.0189	0.047445	**0.0500**	0.0007
Kaolin	2.51	0.0148	0.0028	0	**0.0123**	0.00038	16.436	0.0060	0.212195	**0.0852**	0
Dolomite	6.39	0.0154	0.0139	0	**0.0166**	0.00088	2.307	0.0254	0.476908	**0.8367**	0
Bone earth	24.66	0.0091	0.1052	0	**0**	0.00062	0.973	0.0168	0.200482	**0**	0

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Table 2. Continued.

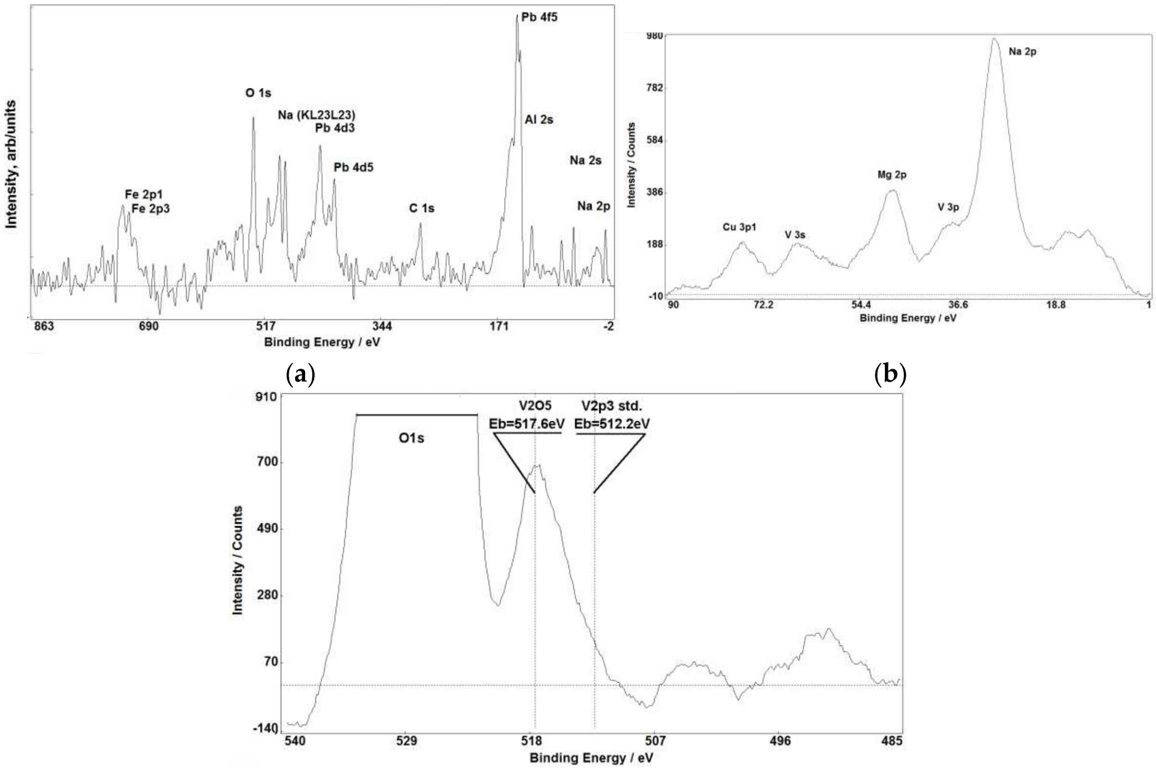
Substance	Zn	Zr	Li	B	Be	Ce
Feldspar	0	0	**0.121**	**0.0073**	**0.00044**	**0**
Pegmatite	0.0066	0	**0.029**	**0.0297**	**0.000843**	**0**
Clay	0.0094	0.000661	**0.365**	**0.0393**	**0.000834**	**0**
Kaolin	0	0.001361	**0.084**	**0**	**0**	**0.00085**
Dolomite	0	0	**0.123**	**0.0131**	**0**	**0**
Bone earth	0.0633	0	**0**	**0**	**0**	**0.002124**

The method for calculations the main and impurity elements concentrations from SIMS data that was used in this research is, of course, semi-quantitative in nature but it is quite suitable to determine compositions of ceramic art items including porcelain and to answer questions about their origin time and location including raw materials for their fabrication. At least this approach has a much greater physical meaning than widely used in the art ceramics archaeometry [19–21]scatter plots of characteristic peaks intensities for various elements I(A) vs. I(B)without corrections on their yield cross-sections.

3.2. XPS studies

Figures 1–6 are presenting some XPS spectra obtained from powders under study. It is necessary to emphasize that enough big escape cross-section of photoelectrons for several elements detected by XPS in the samples (see Figure 1(a, b), Figure 3 (a, b), Figure 7(a, b)) makes XPS partly comparable with SIMS in small impurities determination.

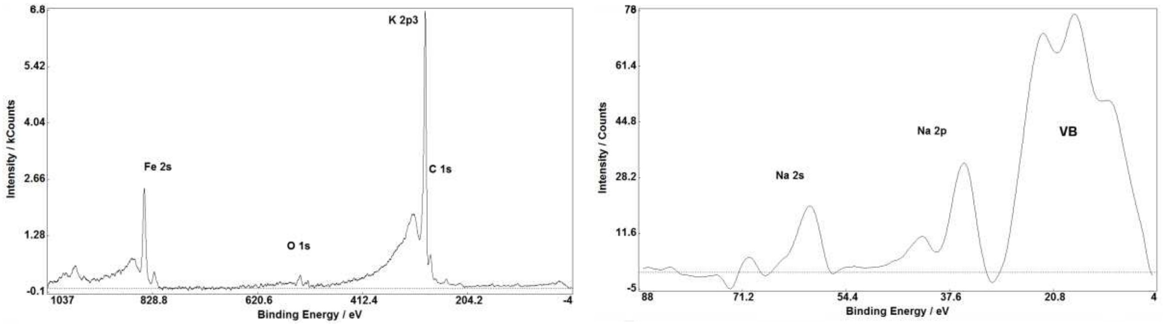
Also the subjects of high importance are oxidation degrees of elements in substances that can be revealed through analysis of chemical shifts of characteristic XPS lines. This information is critical to characterise solid objects including ceramics.



(**a**) (**b**)

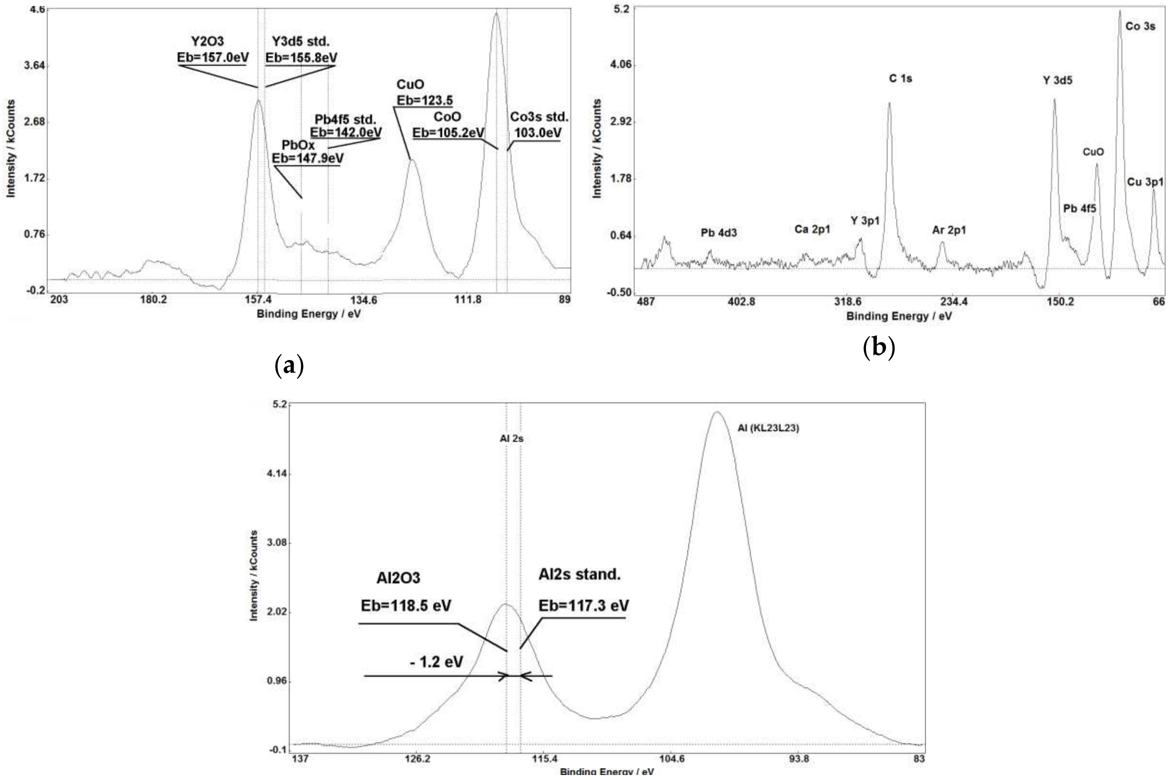
(**c**)

Figure 1. XPS spectra obtained from feldspar: (**a**) Part of the survey spectrum; (**b**) Region with Cu, V, Mg, Na lines; (**c**) V 2p region.



(**a**) (**b**)

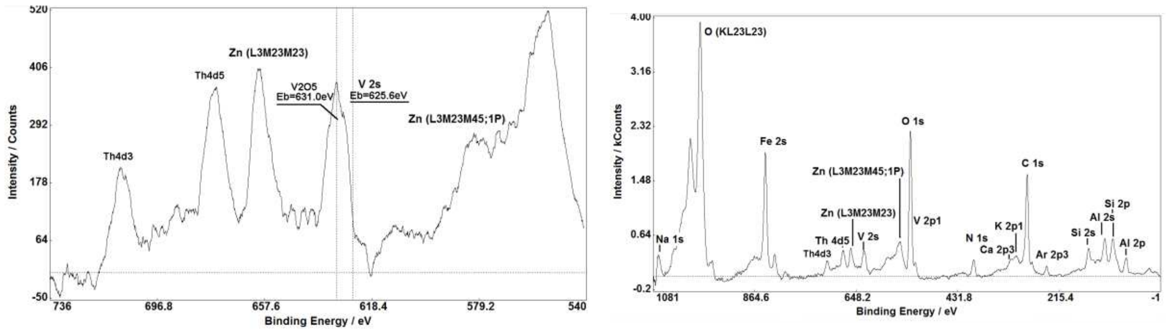
Figure 2. XPS spectra obtained from pegmatite: (**a**) Survey spectrum with strong Fe and K lines; (**b**) Na 2s — Na 2p region.



(**a**) (**b**)

(**c**)

Figure 3. XPS spectra obtained from Vesco-prima clay.



(**a**) (**b**)

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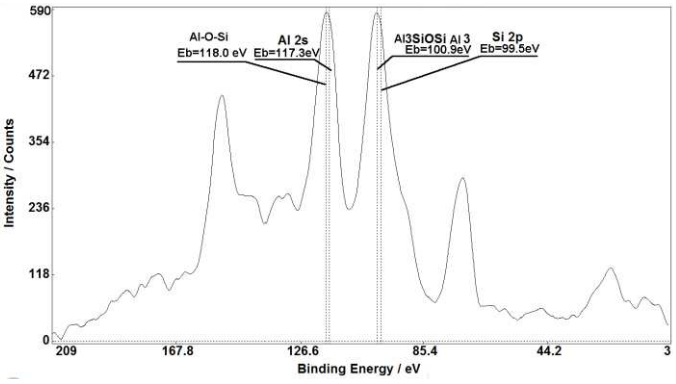
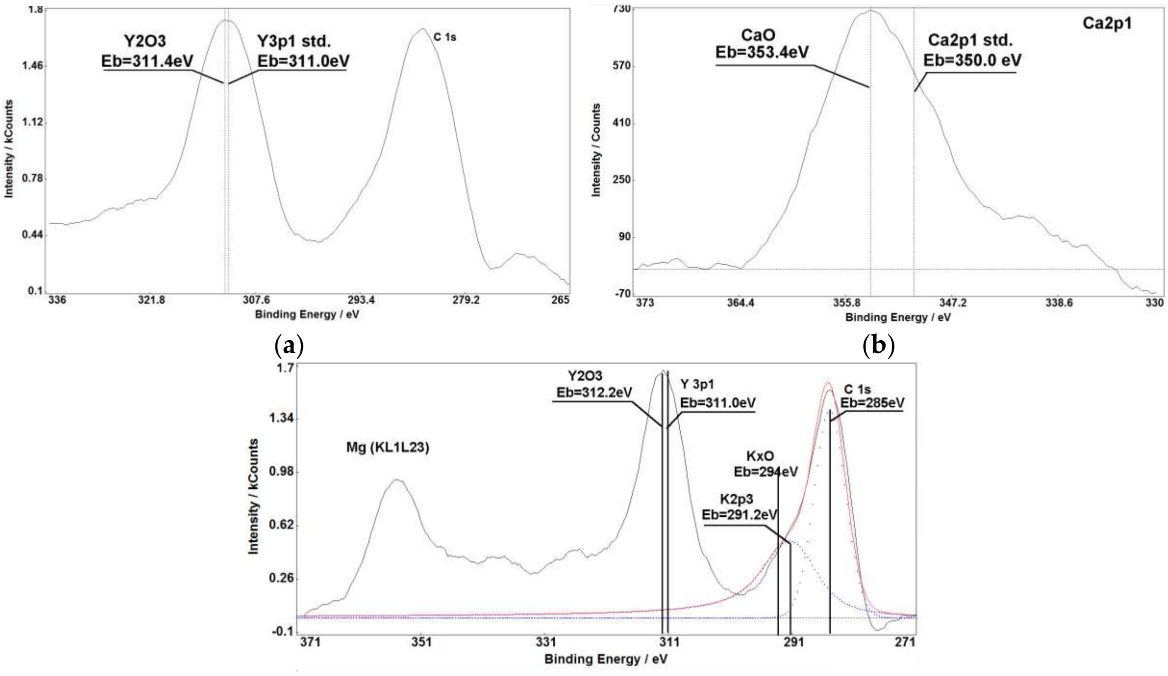


(**c**)

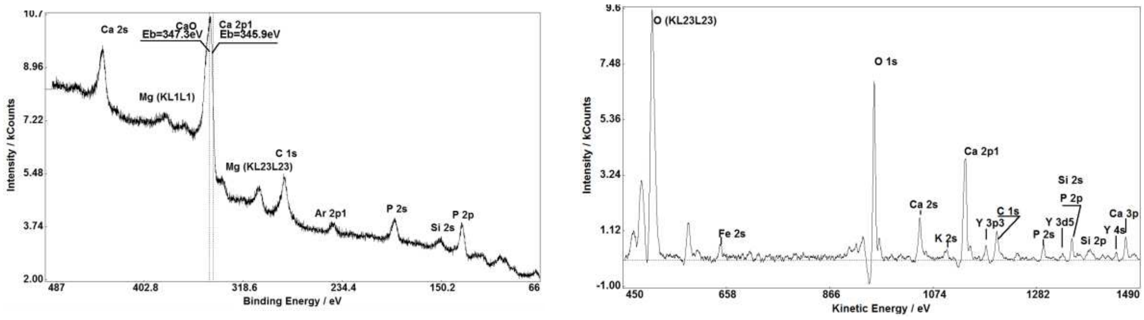
Figure 4. XPS spectra obtained from kaolin.



(**a**) (**b**)

(**c**)

Figure 5. XPS spectra obtained from dolomite.



(**a**) (**b**)

Figure 6. XPS spectra obtained from bone earth.

Figures 3 (c), 4 and 5 demonstrate that chemical shifts of photoelectron lines allow us to accurately determine oxidation states of various elements in raw materials used in porcelain fabrication. Intensities of XPS lines and their chemical shifts allow to establish presence of simple and multicomponent compounds with stoichiometric and non-stoichiometric relations between elements.

The combined application of SIMS and XPS surface analysis methods allows to determine the characteristic features of ceramic goods on their fabrication time, location, and technology that cannot be resolved by commonly used methods for composition and structure analysis. In this case the advantages of these methods such as high value of photoelectrons escape cross-section for heavy (Ba, La, Ce, Pr, Nd, Th, Tb, Gd, Sm, Eu, Bi, Pb) elements and possibility to measure oxidation degrees together with SIMS's high sensitivity to small impurities and determination isotopes relations are fully realised. All these features allow to build the fingerprint of ceramic work-piece and to attribute the sample. It is very interesting that XPS with generally lower sensitivity than SIMS and XRF has detected thorium in the kaolin sample (see Figure 4 (b)) that was not detected by SIMS in spite of its very high sensitivity to small concentrations. Most probably it can be explained by high mass of Th atoms decreasing probability of Th^+ secondary ions emission together with very high photoelectrons yield cross-section up to 23.94 [19]. So the combined application of several surface analysis methods is increasing the reliability of samples composition measurements. Namely, this is a necessary requirement for attribution art items in comparison with subjective visual and stylistic attribution by art history experts.

Meanwhile one can ask about the applicability of these surface analysis methods requiring ultrahigh vacuum equipment for studies art ceramics items that can have enough big dimensions when the most of electron and secondary ions spectrometers can study samples about several centimetres. First of all, art items coming to conservation labs are often fragmented, and it is possible to select samples with proper size as we already did studying Dutch tiles [23]. Secondly, there are no technical limitations to build a spectrometer combining the set of surface analysis methods with enough big work chamber and sample manipulation system, and such system could be built on demand when rather big array of information that can be used for ceramic art items expertise by surface analysis methods will be accumulated.

4. Conclusions

The combined application of SIMS and XPS surface analysis methods allows to determine the characteristic features of ceramic goods on their fabrication time, location, and technology that cannot be resolved by commonly used methods for composition and structure analysis. In this case the advantages of these methods such as high value of photoelectrons escape cross-section for heavy (Ba, La, Ce, Pr, Nd, Th, Tb, Gd, Sm, Eu, Bi, Pb) elements and possibility to measure oxidation degrees together with SIMS's high sensitivity to small impurities are fully realised. All these features allow to build the fingerprint of ceramic work-piece and to attribute it.

It is evident that all elements found in raw stuff are transferred into the bulk of final porcelain goods so obtained data on relations of elements and their chemical state could be used for detection modern counterfeit of historical porcelain and for attribution art ceramic items at conservation efforts.

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