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An X-ray spectrometry and absorption spectroscopy study of blue-and-white glazes from ancient Chinese porcelains

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Abstract

Blue-and-white Chinese porcelains become very appreciated in Europe in the 16th century, following the maritime contact established with China by the Portuguese navigators. The trade to Europe was intense along the 17th century and nowadays both museums and traders face the need to ascertain the authenticity of many art objects through non-destructive tests.
Archaeological findings can appreciably contribute to date ancient Chinese porcelains as proven by various approaches published in the last decade. Therefore, a study of blue-and-white porcelain fragments recovered from recent excavations in Portugal was carried out by non-destructive laboratory X-ray fluorescence spectrometry (XRF-WDS). Once the composition of cobalt blue pigments used in ancient Chinese glazes has changed between the 14th and the 17th century, ratios of main chemical components (Mn/Co and Fe/Co) and trace elements are relevant guide-lines to establish the porcelain manufacture period; according to obtained data, studied porcelain fragments were attributed to the late 16th (with high Mn and Fe contents) and medium 17th century, thus validating the manufacture date advanced by Art Historians on the basis of stylistic features.
Non-invasive X-ray absorption spectroscopy using synchrotron radiation was previously applied to study Co 1*s* XAFS spectra from these ancient blue-and-white Chinese glazes, confirming the expected valence state (2+) of blue-coloring cobalt ions in tetrahedral coordination. An extension of such study to the near-edge spectral region (particularly, pre-edge details) is now presented and discussed by comparing Co *K*-edge XANES data from glazes with spectra collected from model compounds, including blue cobalt pigments.

Key-words: blue glazes; XRF-WDS; Chinese porcelains; cobalt speciation; XANES

Introduction

Following a long tradition of pottery manufacture, China is recognized as being the first porcelain producer about two thousand years ago. After the Portuguese navigators launched the maritime route to China in the beginning of 16th century, the trade of blue-and-white porcelains became more and more intense during the 17th century once such peculiar and fine ceramic materials were not previously accessible to Europeans.

Both Portuguese and Dutch played an important role in this early trading of Chinese porcelains and ascertaining the authenticity of many such imported objects has become a demanding task for archaeologists, art historians and scientists devoted to cultural materials. Exclusively non-destructive methodologies can be used in such studies and non-invasive techniques based on X-rays – namely, X-ray fluorescence spectrometry for the chemical characterization and X-ray absorption spectroscopy to ascertain the speciation state and the coordination environment of pigmenting elements – are particularly suitable to distinguish between forged and true ancient Chinese blue-and-white porcelains.

Problematic

Ancient Chinese porcelain shards have been the object of recently published compositional studies in which analytical techniques based on neutrons (namely, PIXE [1-3]) and photon beams – either laboratory X-rays [4,5] or synchrotron radiation [6] – were applied to ascertain production periods and sites. It is known for long [7] that a shift from imported arsenic-rich Persian cobalt-based pigments towards native Chinese blue pigmenting ores – asbolane or asbolite, a cobalt-containing manganese wad – has occurred during the early Ming Dynasty (AD 1368-1644). This fact rendered possible to outline a dating criterion based on the presence or absence of arsenic plus a combination of Mn/Co and Fe/Co ratios in the glaze.

Cobalt and copper in adequate valence state and suitable coordination environment are the common pigmenting agents of ancient blue glazes, being employed separately or added together to the siliceous matrix in the convenient proportion to attain the desired tonality.

The blue pigmenting properties of cobalt (2+) ions in tetrahedral coordination were established forty years ago for Thenard's blue – ideally the double oxide $CoAl_2O_4$ with spinel-type crystal structure [8] – and were recently reappraised for various cobalt pigments [9]. Beyond ascertaining the bulk chemistry of ancient Chinese blue glazes it is therefore challenging to verify and validate the cause of coloring through the study of formal valence(s) and coordination(s) of cobalt in those ancient glazes.

Once the speciation sate of chromophore elements controls the final coloring effect, a particularly suitable technique to interpret pigmenting performance through non-invasive assays is X-ray absorption spectroscopy using synchrotron radiation. The analysis of both near-edge features (XANES) and extended fine structure (EXAFS) of absorption spectra has been extensively used to study either chromophore ions or modifier elements in ancient glassy materials, with a remarkable success in tile glazes [e.g., 10-13]. A previous XAFS study was undertaken to characterize cobalt speciation plus coordination and tentatively contribute to date a set of seven fragments of Chinese porcelains recovered during recent archaeological excavations when rehabilitating the 14th century Monastery of Santa Clara-a-Velha at Coimbra, central Portugal, and when expanding the underground through Lisbon Old-City [14]. The results of extending such spectroscopic study to a larger group of fifteen Chinese blue-and-white porcelain fragments are described with emphasis on the analysis of pre-edge details and edge features of XANES spectra. Bulk chemical data obtained by non-invasive X-ray fluorescence spectrometry in wavelength dispersive mode (XRF-WDS) are presented and discussed in relation to manufacture dating.

Experimental

The visual appreciation of collected shards allowed to select for the chemical-plus-spectroscopic study a set of Chinese porcelains supposedly manufactured in the 16th and 17th century, that is, in the late Ming period (1368-1644).

Figure 1 reproduces some studied porcelain fragments with indication of the sample reference number given in the archaeological inventory and provisionally dated last quarter of 16th century. Typical Chinese decorations are seen either in the interior of dishes (*camellias* in 17 and *fallow-deers* in 435) or in the borders (*Ruyi* motive in 436 and 461, two porcelain objects displaying very different body cross section for identical glaze thickness); sample 20 is a fragment of a *Kraakporselein* – the Dutch denomination stemming from *Carraca*, the type of Portuguese ship used in the commercial trade with China along the 16th-17th century.

A wavelength-dispersive X-ray fluorescence *(*XRF-WDS) spectrometer Philips PW1400 with a rhodium tube and a LiF200 analyzing crystal was used for the non-destructive bulk chemical study by irradiating the whole porcelain shard in the case of small-sized samples and a very small fragment taken from larger pieces. Fixed-time counting was carried out over the *K*α diagnostic peaks of the relevant glaze components, the transition metals Mn , Fe , Co , Ni , Cu , Zn , and K plus Sn . In view of the interference of Pb *L*α line on As *K*α, the *K*β peak of arsenic and the *L*γ peak of lead were also systematically measured to ascertain the presence of each element. Measurement of the spectra background was carried out at various 2θº according to the positions of diagnostic peaks (21.5º for lead and arsenic, 50.0º for the transition metals and 134.0º for tin and potassium). Co 1*s* X-ray absorption spectra were collected using the instrumental set-up of beam line BM-29 at the European Synchrotron Radiation Facility (ESRF in Grenoble/France) by directly irradiating the surface of the glazed debris and detecting the fluorescence yield with a germanium detector. A cobalt metal foil was used for energy calibration and the energy resolution ΔE/E of the beamline at the time of the experiment was about 10^{-4}, that is, ~ 0.8 eV at the cobalt absorption edge.

To model cobalt speciation and coordination environment, double oxides with known crystal structure and commercial blue pigments which phase constitution was previously checked by X-ray diffraction were irradiated as pellets and the transmission absorption spectra were collected in total electron yield (TEY) mode.

Results and discussion

Table 1 lists the chemical data obtained for the fifteen studied samples through the non-invasive XRF-WDS assay.

In most porcelain fragments the copper content of the glazes is low comparatively to cobalt, with the exception of sample 442 that belongs to the set of five lead-rich glazes assigned in Table 1. The presence of arsenic is ruled out in the other ten glazes due to the close values of the count-rate obtained at Pb *L*γ, As *K*β and the energy-coincident As *K*α plus Pb *L*α emission lines. Simultaneously, clearly distinct values of Mn/Co and Fe/Co ratios were obtained for these two sample sub-sets despite all the analyzed porcelain glazes display a Fe/Co ratio higher than Mn/Co.

Concerning the blue-and-white Chinese porcelain shards collected in the Monastery of Santa Clara-a-Velha, at Coimbra, (samples 94 and 95) actual results are in agreement with data from a recent μ-EDXRF study carried out with a portable apparatus on a large set of archaeological fragments [15]. Co *K*-edge XANES spectra collected from the blue glazes (figure 2) display the same general trend for all porcelain fragments: a quite intense pre-edge feature centered at ~7709 eV, an edge energy indicative of a dominant divalent state for the cobalt ions (7718 eV) and poorly defined edge features.

Corresponding spectra collected from model oxides – $Co\,Al_2O_4$, Co_2SiO_4, “Co_2SnO_4” (cerulean blue), Co_3O_4 – display distinct near-edge layouts as expected from the presence of exclusively Co^{3+} ions in the last one and Co^{2+} ions with distinct close oxygen environments in the double oxides (tetrahedral coordination in the first, octahedral in the second and tetrahedral plus octahedral in the third). Figure 3 reproduces the first derivatives of Co 1*s* XANES spectra collected from the double oxides, thus emphasizing the variability of edge features obtained for these compounds.

After resolving the pre-edge spectral region using Fityk program [16], the contributing features so-obtained differ slightly in energy position and intensity (figure 4): a dominant contribution centered at 7709 eV due to Co^{2+} bordered by two minor contributions when these ions are present in tetrahedral coordination (non centro-symmetric environment) and a single one at higher energy for octahedral coordination or two significant contributions if Co^{3+} ions are also present.

By comparing the resolved details of Co *K*-edge XANES spectra of blue-and-white glazes from porcelain fragments (illustrated by figure 5), the prevailing tetrahedral environment around the $3d^7$ transition metal ion Co^{2+} in the Chinese glazes becomes clearly apparent, in accordance with data previously extracted from EXAFS spectra [14]: mean coordination number 4.4 ± 0.6 Å and Co-O distances close to 2.0 Å.

Conclusions

Considering the analytical results recently obtained by synchrotron X-ray fluorescence (SR-XRF) [6] and PIXE [2,3] for Chinese porcelains manufactured in the Ming period (AD 1368-1644), actual Mn/Co and Fe/Co ratios, combined with the absence of arsenic, corroborate the advanced manufacture dating anticipated by Art-Historians for the studied blue-and-white Chinese porcelains (late 16th to early 17th century, Table 1).

Differences in pre-edge features of XANES spectra collected from model oxides may be explained by the local symmetry of cobalt ions: Co^{2+} with a regular tetrahedral environment and site symmetry $\bar{4}3m$ in the spinel-type double oxides $Co\,Al_2O_4$ and “Co_2SnO_4” and single oxide Co_3O_4 and non-coloring octahedral Co^{2+} with two different site symmetries ($\bar{1}$ and *m*) in Co_2SiO_4 (olivine-type structure). Further details observed in the XANES spectrum of spinel-type single oxide stem from Co^{3+} ions in octahedral coordination.

Indeed, *K*-edge XANES spectra of 3*d* transition metals arise from electronic transitions from the 1*s* core state to the 4*p* conduction band and the energy position of the absorption edge was recently questioned as a measure of the oxidation state due to the complex electronic structure of these elements [17]. Pre-edge details stem mainly from quadrupole transitions to 3*d* empty states and when the inherent inversion symmetry is broken (as is the case for Co^{2+}, a high spin $3d^7$ ion with filled e_g and t_{2g} orbitals), local 3*d* 4*p* wave function mixing allows for dipole transitions to occur, thus intensifying the pre-edge features [18]. These considerations explain actual spectroscopic results obtained for both the studied model compounds and the Chinese porcelain samples. Cobalt should then have a dominant role of chromophore and a minor network-former character in the glaze of ancient Chinese porcelains with tetrahedral Co^{2+} ions being responsible for the blue coloring [19], although the higher than 4 coordination value could account for a network-modifying situation of non-coloring pseudo-octahedral Co^{2+} ions filling higher coordination sites within the silica-rich glassy matrix.

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Figure captions

Figure 1. Illustrative examples of studied blue-and-white Chinese porcelain fragments.

Figure 2. Co *K*-edge XANES spectra of blue glazes from porcelain fragments displaying broad (a) and detailed (b) edge features and showing a poorly resolved layout (c).

Figure 3. First derivatives of Co *K*-edge XANES spectra collected from double-oxide model compounds enhancing the differences in edge features.

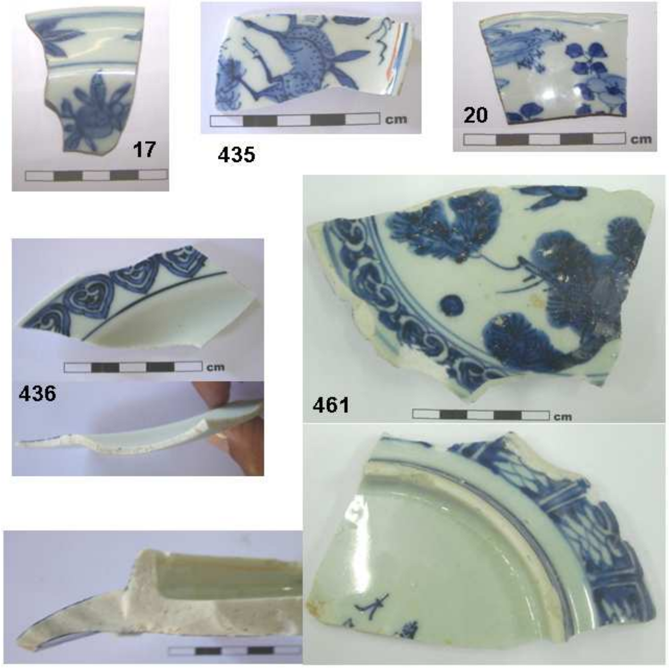
Figure 4. Comparison of resolved pre-edge details in Co 1*s* XANES spectra of model oxides.

Figure 5. Illustrative examples of resolved pre-edge details in Co 1*s* XANES spectra from archaeological shards of blue-and-white Chinese porcelains recovered at various places in Lisbon Old-City.

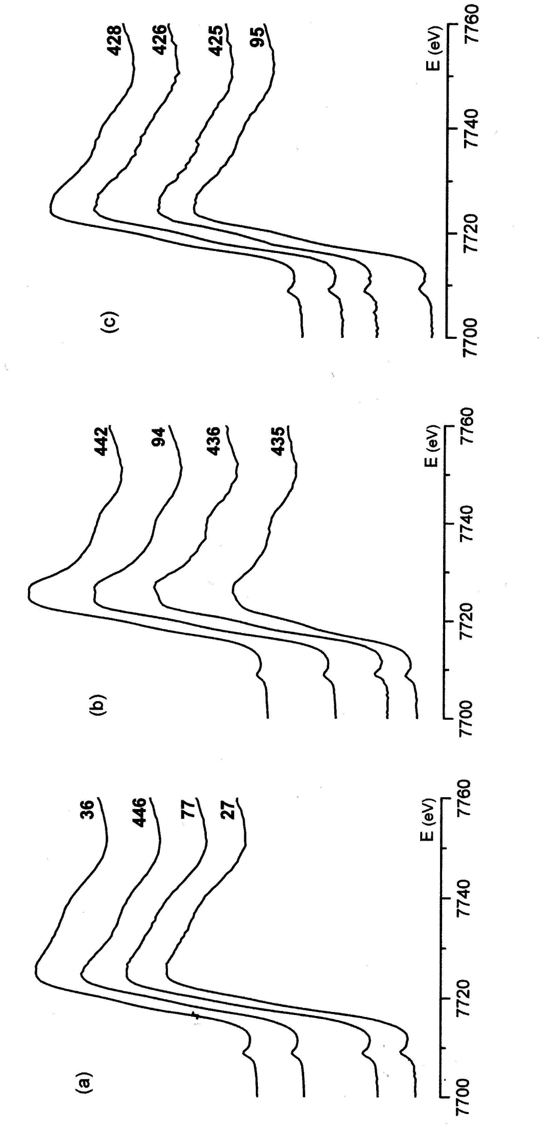
Table 1 . Chemical data obtained by X-ray fluorescence spectrometry in wave-length dispersive mode (FRX-WDS)

Sample nr.	**27**	**36**	**77**	**446**	**442**	**94***	**435**	**436**	**20**	**17**	**95***	**425**	**426**	**428**	**461**
Preliminary dating	*XVII century, first half*					*XVI century, second half - third quarter*									
Element (2θº)	Counts-per-second (cps) at the angular position														
Background (134.0)	42	98	149	50	61	256	32	46	1 337	520	196	43	45	136	609
K *K*α (136.8)	44 395	24 721	26 792	4 241	2 370	70 570	5 346	5 753	286 200	107 088	54 771	6 252	4 433	36 918	128 250
Sn *L*β (114.4)	341	2 076	4 234	162	571	334	68	49	5 358	1 444	656	66	55	274	2 844
Mn *K*α (62.97)	389	640	2 103	378	409	14 376	3 150	5 223	20 292	8 382	22 229	8 557	4 524	47 638	28 348
Fe *K*α (57.52)	7 486	41 417	33 350	17 024	6 501	102 270	25 798	27 269	82 262	40 038	104 162	9 836	27 001	67 388	47 452
Co *K*α (52.80)	2 824	26 556	13 244	13 868	2 016	5 522	1 421	1 569	6 896	1 623	3 649	1 841	1 414	11 073	9 058
Background (50.00)	311	478	1 445	304	308	1 084	523	609	987	324	916	211	587	566	488
Ni *K*α (48.67)	1 380	10 374	4 619	8 603	1 095	2 588	515	1 194	2 676	2 820	2 522	719	699	4 783	1 893
Cu *K*α (45.03)	954	1 395	3 755	759	18 551	2 969	1 634	1 700	2 643	1 410	2 523	361	1 704	2 045	1 452
Zn *K*α (41.80)	552	1 120	2 413	535	591	1 873	2 213	2 183	2 149	804	3 445	340	2 234	1 421	1 654
Mn / Co ratio	*< 0.1*	*< 0.1*	*0.1*	*< 0.1*	*0.1*	***3.0***	***2.9***	***4.7***	***3.3***	***6.2***	***7.8***	***5.1***	***4.8***	***4.5***	***3.3***
Fe / Co ratio	*2.9*	*1.6*	*2.7*	*1.2*	*3.6*	***22.8***	***28.2***	***27.8***	***13.8***	***30.5***	***37.8***	***5.9***	***31.9***	***6.4***	***5.5***
Co / Cu ratio	*3.9*	***28.4***	*5.1*	***29.8***	*0.1*	*2.4*	*0.8*	*0.9*	*3.6*	*1.2*	*1.7*	***10.9***	*0.7*	***7.1***	***8.9***
Co / Ni ratio	*2.4*	*2.6*	*3.7*	*1.6*	*2.2*	*2.9*	*-*	*1.6*	*3.5*	*0.5*	*1.7*	*3.2*	*7.4*	*2.5*	*6.1*
As *K*α+**Pb** *L*α (34.00)	127 150	173 715	683 366	91 633	40 813	2 163	1 086	1 051	2 508	872	2 188	296	959	1 531	1 388
As *K*β (30.45)	541	1 822	4 639	1 437	490	2 063	925	954	2 105	684	1 875	275	948	1 144	1 055
Pb *L*γ (24.07)	8 137	15 438	49 944	6 655	3 388	2 359	951	1 015	2 455	864	2 089	273	1 025	1 208	1 253
Background (21.50)	219	568	1 383	225	297	2 535	943	928	1 337	850	2 242	277	1 010	1 252	1 367

* Samples collected at the Monastery of Santa-Clara-a-Velha in Coimbra. The remaining samples were collected in the area of Lisbon Old-City

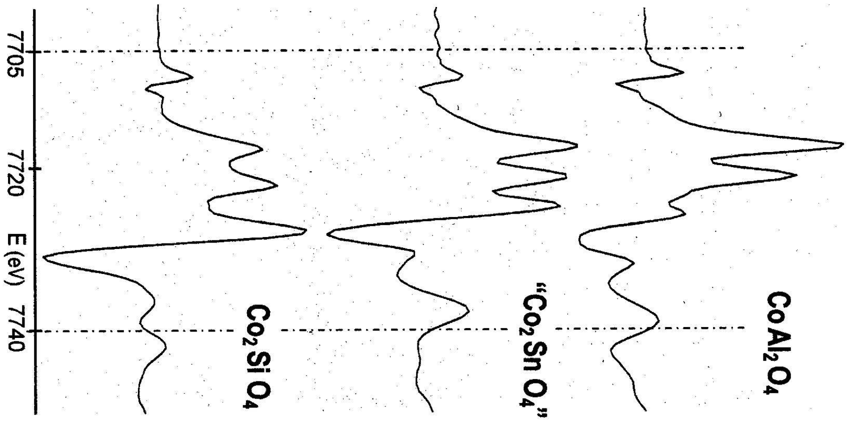


Illustrative examples of studied blue-and-white Chinese porcelain fragments.
254x190mm (96 x 96 DPI)

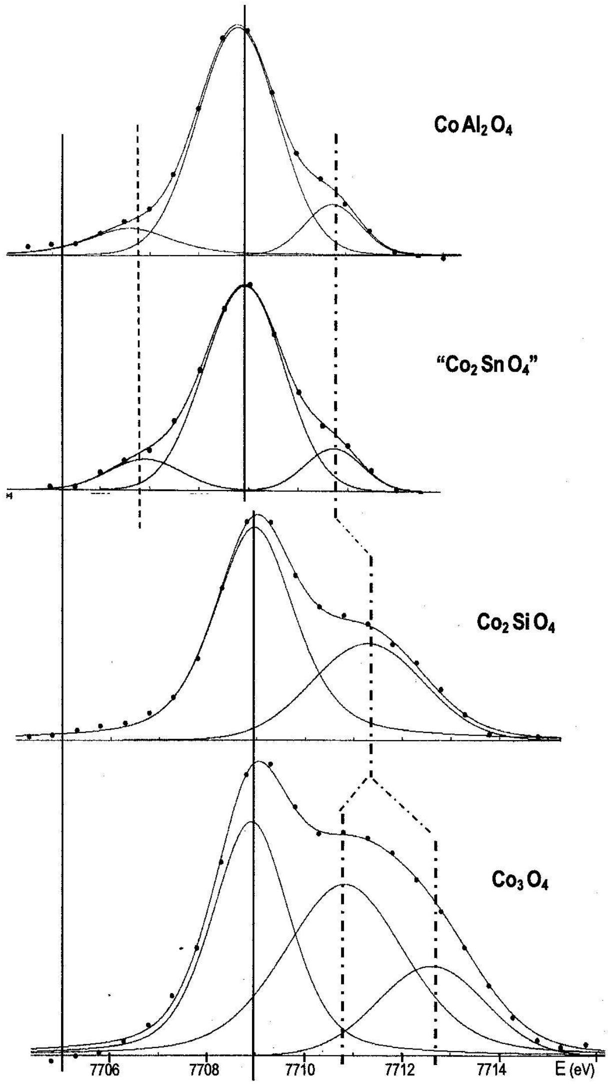


Co K-edge XANES spectra of blue glazes from porcelain fragments displaying broad (a) and detailed (b) edge features and showing a poorly resolved layout (c).

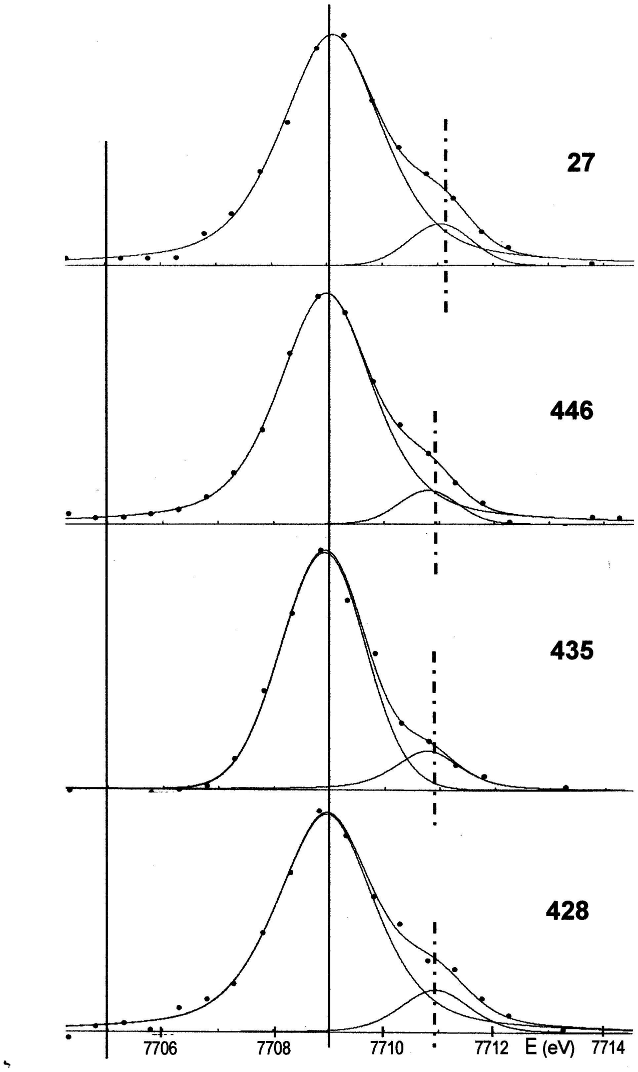
449x938mm (96 x 96 DPI)



First derivatives of Co K-edge XANES spectra collected from double-oxide model compounds enhancing the differences in edge features.
507x287mm (96 x 96 DPI)



Comparison of resolved pre-edge details in Co 1s XANES spectra of model oxides.
672x1088mm (96 x 96 DPI)



Illustrative examples of resolved pre-edge details in Co 1s XANES spectra from archaeological shards of blue-and-white Chinese porcelains recovered at various places in Lisbon Old-City.
589x958mm (96 x 96 DPI)