

FREE XRF SPECTROSCOPY DATABASE OF PIGMENTS CHECKER

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Abstract

Pigments Checker is a collection of swatches of historical pigments that offers art professionals, conservation scientists, conservators and fine art photographers, a tool to evaluate and test their imaging and spectroscopic methodologies for pigment identification. "Pigments Checker Free Spectra Database" is an ongoing project that wants to thoroughly characterize each pigment in the collection with a series of spectroscopic and imaging techniques and to make the data open access. This paper presents the free and downloadable database of XRF spectra, adding to the reflectance spectral database already published. The XRF analysis is in agreement with the information provided by the pigments' manufacturers since all of the pigments have XRF spectra consistent with the expected elemental content reported in literature. In addition to elemental characterization by XRF, future analysis with Raman, FT-IR and XRD will be pursued in order to achieve a broader characterization of the pigments.

Keywords: X-Ray Fluorescent Spectroscopy; Artefact heritage; Paint Analysis;
Pigments Checker

Introduction

Conservation scientists collaborate with museums, libraries and conservation laboratories to provide scientific examination of works of art and archaeology. Non-invasive and non-destructive methods are preferred to avoid sampling. There are spectroscopic methods (such as Raman spectroscopy [1], XRF spectroscopy [2], neutron techniques [3] and mobile atomic force microscopy [4]) and imaging methods (such as Technical photography [5], reflectance transformation imaging (RTI) [6], Terahertz [7] and Multispectral Imaging (MSI) [8]).

The CHSOS (Cultural Heritage Science Open Source) initiative promotes innovative, affordable and sustainable technologies for art examination in order to serve the large art professional community, such as conservators, art appraisers, art photographers and archaeologists who wish to introduce budget scientific diagnostics methods into their workflow. CHSOS develops and disseminates each year an affordable version of a scientific tool for art examination: Technical Photography in 2013 [9], an affordable Infrared Reflectography system in 2014 [10] and a low-cost Multispectral Imaging system in 2015 [11].

Recently, CHSOS has launched Pigments Checker, a collection of swatches of historical pigments to offers art professionals, conservation scientists, conservators and fine art photographers, a tool to evaluate and test their imaging and spectroscopic methodologies for

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pigments identification. Pigments Checker has been acquired by a number of institutions where scientists and conservators have found it useful for their professional practice and research.

CHSOS started the “Pigments Checker Free Spectra Database” project in 2015 in order to make Pigments Checker a more valuable tool for scientific research in art conservation. An international team of laboratories and research groups involved in scientific art examination have worked with CHSOS to create a *Free and Downloadable* spectral database of the pigments in Pigments Checker: Reflectance, XRF, Raman, FTIR and XRD. The database is available for download from the Pigments Checker webpage [12]. The spectroscopic data confirm the composition and provide details on the actual chemical composition and structure of the pigments. Reflectance spectra are already part of this database [13]. This paper presents the new XRF database and discusses the results.

While reflectance spectroscopy systems are among the most affordable spectroscopic methods, XRF spectroscopy is the most used as a non-invasive tool to investigate art and archaeology, such as lithic artifacts [14], archaeological glass [15], pottery [16] and metal alloys [17]. Its adoption by a large number of art professionals and institutions is due to its mobile and portable implementation [18]. Its most frequent application is to define the elemental composition of pigments used in works of art, such as easel paintings [19], mural paintings [20], illuminated manuscripts [21] and inks on paper documents [22].

There are a number of XRF studies of works of art which make reference to XRF pigment databases belonging to their institutions. Yet, the databases are not published [23-26]. There is only one project that makes the spectra available online, but just as images [27] and, generally, identification by XRF is performed by consulting scientific literature [28-31], which may be the reason why there are few published XRF spectra databases.

Experimental

Pigments Checker

XRF spectra were collected on the 54 pigments in Pigments Checker v.2 and on 4 pigments that will be added in v. 3. The 58 pigments are listed in Table 1. Pigments Checker is a collection of swatches of historical pigments that have been applied using gum arabic (Fig. 1). The pigments are milled into the binder which is added as needed for each pigment and applied with a brush. Among all the pigments and their varieties ever used in art, these selected pigments represent the most used ones from antiquity to early 1950's. A swatch of just gum arabic is added as a reference. Pigments are painted over cellulose and cotton cardboard, which is acid and lignin free not treated with optical brighteners, slightly fluorescent in the UV and reflects infrared radiation. Two cross-hairs (0.2mm and 0.4mm) are printed on each swatch of cardboard before paint application in order to evaluate each pigment's transparency to infrared imaging. Pigments Checker (v.2.1, 2015) is currently composed of 54 commercially available pigments listed in Table 1 together with their name and product code. Suffix to the product code K, C, or Z indicate respectively Kremer, Cornelissen and Zecchi, pigments sellers.

XRF spectroscopy

Samples were prepared for XRF analysis by placing between 200 – 400mg of pigments into plastic 5mL conical vials. Because of this configuration, the excitation X-ray had a greater depth than 1cm of pigment in which it could penetrate. A Spectro Midex LD X-ray fluorescence spectrometer was used to collect the spectra. The system consists of a motorized XYZ sampling stage mounted within a shielded container. An air-cooled 30W Mo anode X-ray tube generates a 0.5mm collimated X-ray excitation beam, which is focused onto a 1mm square spot on the sample surface. A Peltier-cooled Si drift detector acquires the X-ray fluorescence signal with a working distance of 20mm and measurements conducted in ambient atmosphere. As a result, low atomic number elements cannot be detected and atmospheric argon is present in the

resulting spectra. XRF spectra were collected for 180 seconds with the Mo anode operating at 45kV and 0.5mA.

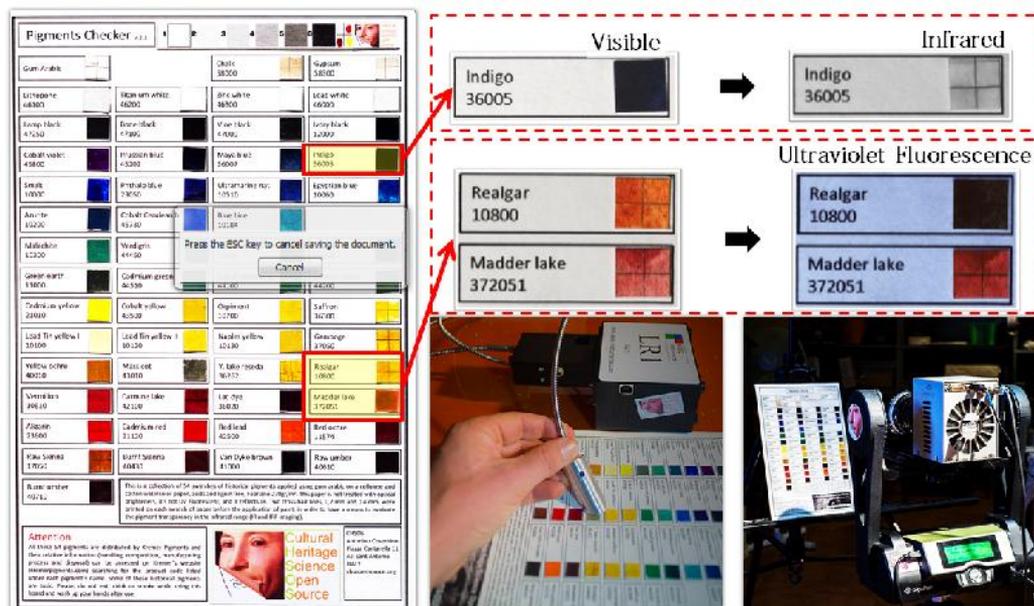


Fig. 1. Pigments Checker. It is designed for pigment identification by imaging and spectroscopic analysis.

Table 1. Pigments. Name (product name, color index, product code), chemical name, XRF data.

Name / product code	Composition	XRF Analysis
BLACKS		
vine black (PBk8) K-47000	amorphous C	traces: Ca, Fe, Ni, Cu, Br, Sr
lamp black (PBk7) K-47250	amorphous C	traces: Ca
ivory black (PBk9) K-12000	amorphous C	traces: Ca, Sr
bone black (PBk9) K-47100	amorphous C	traces: Ca, Fe, Zn, Sr
GREEN		
cobalt titanate green. K-44100	cobalt titanate green spinel	Co, Ti, Ni, Zn, traces: Cr, Ca, Ti, Sr, Ba
viridian K-44250	hydrated chromium oxide	Cr, traces: Ca
malachite K-10300	basic copper(II) carbonate	Cu, traces: Ca, Fe
cadmium green K-44510	barium sulfate, cadmium yellow, phthalocyanine blue	Cd, traces: Zn, Sr, Ca, Cu, Ba
verdigris K-44450	copper-(II)-acetate-1-hydrate	Cu, traces: Ca, Fe
chrome green K-44200	chromium(III)-oxide	Cr, traces: Ca
phthalo green K-23000	copper-phthalocyanine	Cu, traces: Br, Cl
green earth K-11000	glauconite and celadonite	Fe, traces: Ca, Sr
RED		
lac dye K-36020	laccic acid	traces: Ca
madder lake C-LC12061A	rubia tinctorum	traces: Ca
carmin lake K-42100	carminic acid	traces: Ca
alizarin K-23600	dihydroxyanthraquinone	traces Ca
vermilion K-10610	mercury sulfide	Hg
cadmium red K-21120	cadmium selenosulfide	Cd, Se, traces: Zn
red ochre K-11574	iron oxides	Fe, traces: Ca
red lead K-42500	lead(II,IV) oxide	Pb
BROWN		
van dyke brown (NBr8) K-41000	humic acids, iron oxide	Fe, traces: Ca, Zn, Sr
burnt umber (PBr8) K-40710	manganese and iron oxides	Fe, traces: Ca, Mn
raw umber (PBr8) K-40610	manganese and iron oxides	Fe, traces: Ca, Mn
raw sienna (PY 43) K-17050	iron oxides	Fe, traces: Ca
burnt sienna (PR101) K-40430	iron oxides	Fe, traces: Ca

WHITE		
chalk (PW18) K-58000	calcium carbonate	Ca, Sr
zinc white (PW4) K-46300	zinc oxide	Zn, traces: Co
gypsum (PW25) K-58300	hydrated calcium sulfate	Ca, Sr
titanium white (PW6) K-46200	titanium dioxide	Ti, traces: Ca
lithopone (PW5) K-46100	zinc sulfide and barium sulfate	Zn, Ba, traces: Ca
lead white (PW1) K-46000	basic lead carbonate	Pb
BLUE		
smalt (PB32) K-10000	cobalt potassium silicate glass	Co, Pb
cobalt cerulean blue (PB35) K-45730	cobalt stannate	Co, Sn, traces: Ba, Zn
ultramarine (PB29) K-10510	sodium-aluminum-silicate	Traces: Fe and Cu
maya blue (N/A) K-36007	indigo in silicic crystal matrix	Fe
prussian blue (PB27) K-45202	iron-hexacyanoferrate	Fe
azurite (PB30) K-10200	basic copper carbonate	Cu, traces: Fe
indigo (NB1) K-36000	indigotin	Fe, traces: Mn, Zn
egyptian blue (PB31) K-10060	copper calcium silicate	Cu, traces: Fe, Ca
phthalo blue (PB15) K-23050	copper phthalocyanine	Cu, Fe, traces: Ca
cobalt violet (PV14) K-45800	cobalt phosphates	Co
blue bice (PB30) K-10184	basic copper carbonate	Cu, traces: Fe
YELLOW		
gamboge (NY24) K-37050	garcinia hanburyi tree	Ca
naples yellow (PY41) K-10130	lead antimonate	Pb, Sb, Zn, traces: Fe
lead tin yellow I (N/A) K-10100	lead stannate	Pb, Sn
cadmium yellow (PY35) K-21010	cadmium zinc sulfide	Cd, Zn
lead tin yellow II (N/A) K-10120	lead and tin oxides	Pb, Sn
cobalt yellow (PY40) K-43500	potassium cobaltinitrite	Co, traces: Ca
massicot (PY46) K-43010	lead(II)oxide	Pb, traces: Cd, Sn
yellow ochre (PY43) K-40010	goethite	Fe, traces: Ca
Realgar (PY39) K-10800	arsenic sulfide	As, traces: Fe, Zn, Pb, Ag, Sb
orpiment (PY39) K-10700	arsenic sulfide	As, traces: Fe, Zn, Pb, Ag, Sb
yellow lake reseda (NY2) K-36262	reseda luteola	Sn, traces: Fe, Ca, Zn
saffron (NY6) K-36300	saffron	Ca, traces: Ti
NEW		
cobalt blue (PB28) Z-C0953	cobalt aluminate	Co, traces: Ca, Mn
cerulean blue (PB36) Z-C0040	cobalt chromite	Co, Cr, traces: Ca
chrome yellow (PY34) C-LC11053F	lead chromate	Pb, Cr traces: Ca
Bitumen (NBk6) Z-0098	high-molecular hydrocarbons	traces: Ca, Fe, Ni

Results and Discussion

The XRF results were compared with information in the literature regarding each pigment.

Black pigments

The four black pigments (vine black, bone black, ivory black and lamp black) are based on the soot generated from the burning of organic material and represent the most used methods to produce amorphous carbon black pigments. As expected, their XRF spectra only show traces of non-characterizing elements.

White pigments

The most used white pigments are characterized by heavy elements. Lead white, a basic lead carbonate, shows Pb lines at 10.50 (L), 12.62 (L) and 14.76 (L). Titanium white, titanium dioxide, shows Ti lines at 4.51 (K) 4.93 (K) while zinc white, a zinc oxide, reveals its Zn lines at 8.63 (K) and 9.57 (K). It also show traces of Co, a known impurity for this pigment, with lines at 6.93 (K) and 7.65 (K) [32] (Fig 2). Lithopone, a mixture of zinc sulfide and barium sulfate, features the Zn lines together with Ba lines at 32.0 (K) and 36.38 (K). Chalk (calcium carbonate) and gypsum (hydrated calcium sulfate) show the Ca lines at 3.69 (K) and 4.01(K) associated with its usual impurity Sr with lines at 14.14 (K) 15.84 (K). In particular, Sr in gypsum is an impurity due to celestine SrSO_4 [33]. Gum arabic powder, used as a binder for Pigments Checker, was also measured and revealed no characterizing lines.

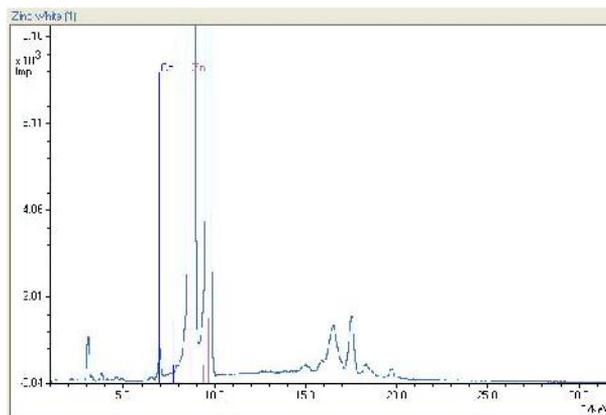


Fig. 2. XRF spectrum of zinc white showing Zn and Co lines.

Blue pigments

The 13 blue pigments can be grouped based on their main characterizing XRF lines. There are four copper-based pigments: azurite, blue bice, Egyptian blue and phthalo blue. All of them show the characterizing Cu lines at 8.04 (K) and 8.90 (K). Azurite and blue bice (in its artificial form) are basic copper carbonates and their XRF spectra also show Fe lines at 6.40 (K) and 7.06 (K) from iron oxides, impurities documented both in the mineral and synthetic forms [34] (Fig. 3). Egyptian blue, a copper calcium silicate, reveals traces of Fe and Ca. Phthalo blue, a copper phthalocyanine, shows traces of Fe and Ca. There are five blue cobalt-based pigments: smalt, cobalt cerulean blue, cobalt blue, cobalt violet, and cerulean blue, each of them showing the Co lines. Cobalt blue, a cobalt aluminate, and cobalt violet, containing cobalt phosphates, feature just Co lines while the other pigments have additional characterizing elements. Smalt, a powdered blue cobalt potassium silicate glass, shows a large Pb signal which can be linked with impurities in the cobalt minerals as well as lead glass in the pigment manufacturing. Cobalt cerulean blue, a cobalt stannate, reveals Sn lines at 25.16 (K) and 28.49 (K) while cerulean blue (cobalt chromite) shows Cr lines at 5.41(K) and 5.95 (K).

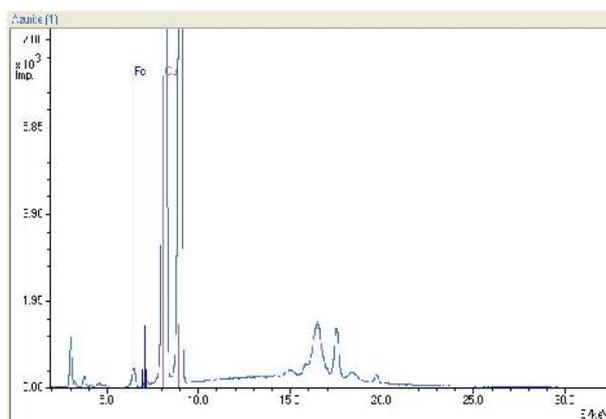


Fig. 3. XRF spectrum of azurite showing Cu and Fe lines.

Prussian blue, an iron-hexacyanoferrate, is the only blue pigment characterized by Fe K and K lines. There are three blue pigments with only light characterizing elements: ultramarine, indigo and maya blue. This XRF system working in open air and at long distance (20mm) is not

capable of detecting the presence of the lighter elements sodium, aluminum, silicon and sulfur that are expected in ultramarine (lazurite). On the other hand, ultramarine contains other minerals, such as calcite and iron pyrites, from which the Fe and Cu traces in the XRF spectrum arise. Impurities in ultramarine have been analyzed extensively for provenience studies [35] (Fig. 4). Indigo and maya blue (indigo in silicic crystal matrix), as expected, do not have characterizing lines.

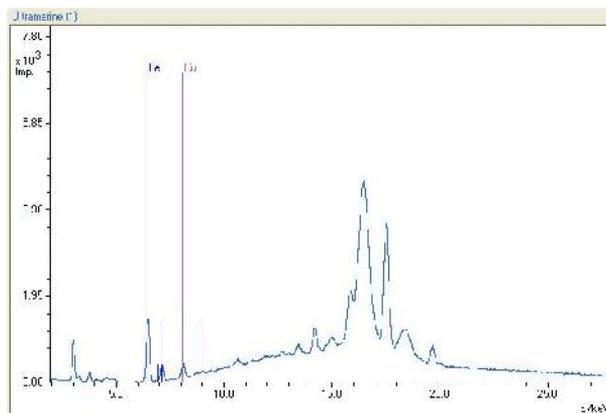


Fig. 4. XRF spectrum of ultramarine showing Fe and Cu lines.

Brown pigments

The six brown pigments are iron-based and all show the Fe lines. While raw sienna and burnt sienna are characterized just by the iron oxides, burnt and raw umber show the Mn lines at 5.89 (K) and 6.49 (K) from their manganese oxides, mostly pyrolusite [36] (Fig. 5). Van Dyke brown (humic acids and iron oxides), and Bitumen (high-molecular hydrocarbons) have respectively small and traces Fe content.

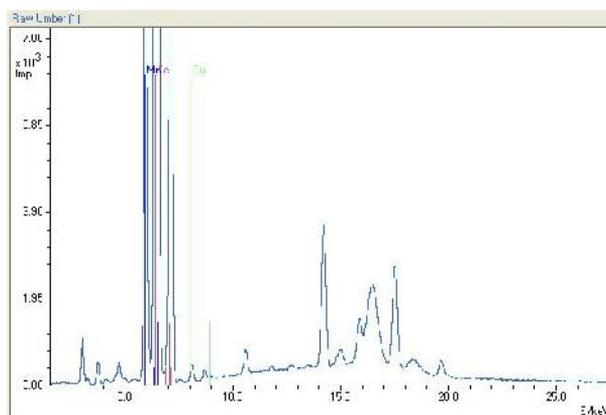


Fig. 5. XRF spectrum of raw umber showing Mn, Fe and Cu lines.

Green pigments

The eight green pigments have a variety of metal characterizing elements. Three are three copper based-pigments. Malachite, a basic copper(II) carbonate, and verdigris (copper(II)-acetate-1-hydrate) have intense Cu lines, while phthalo green, copper-phthalocyanine halogenated (chlorine and bromine), features Cu lines together with Cl lines at 2.62 (K) and 2.81 (K) and Br lines at 11.91 (K) and 13.29 (K) (Fig. 6).

There are two chromium-based pigments characterized by their Cr lines: chrome green (chromium(III)-oxide) and viridian (hydrated chromium oxide). Only cobalt green, a cobalt

titanate green spinel, is a cobalt-based pigment which also shows lines from Ti and Zn. The later could have been added as a modifier (ZnO). Nickel, a known impurity in cobalt minerals, was also observed in cobalt green at 7.47 (K) and 8.26 (K). Green earth, a natural mixture of green iron minerals glauconite and celadonite, features the characteristic Fe lines, while cadmium green, a mixture of barium sulfate, cadmium yellow, phthalocyanine blue, has the characterizing Cd lines at 23.08 (K) and 26.10 (K).

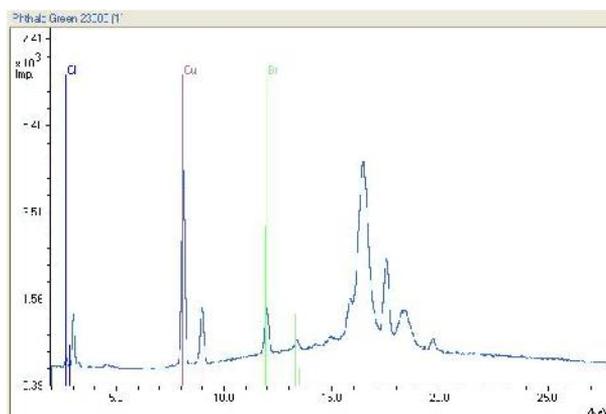


Fig. 6. XRF spectrum of phthalo green showing Cu, Cl and Br lines.

Red pigments

Eight red pigments were analyzed. The red lakes (lac dye, madder lake, carmine lake and alizarin), as expected, show just lines from Ca due to the mordant. Vermilion, mercury sulfide, features the Hg lines at 9.95 (L), 11.87 (L), 13.83 (L). Red lead, lead (II, IV) oxide, shows just Pb lines. Cadmium red, a cadmium selenosulfide, features both Cd and Se lines at 11.20 (K) and 12.50 (K) (Fig 7). Red ochre (iron oxides) is characterized by Fe lines.

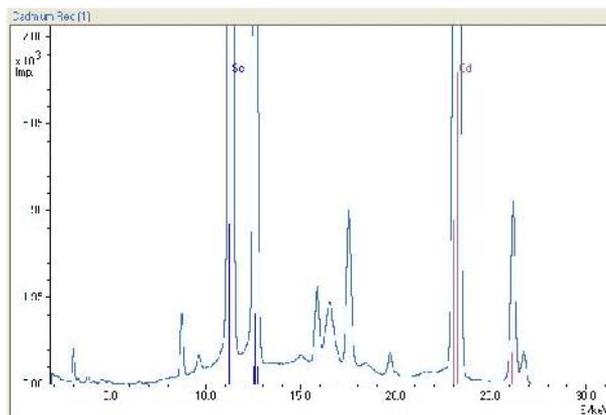


Fig. 7. XRF spectrum of cadmium red showing Cd and Se lines.

Yellow pigments

Lead tin yellow I (lead stannate) and II, lead and tin oxides, feature Pb and Sn lines. Realgar and orpiment, both arsenic sulfides, are identified by the As lines at 10.53 (K) and 11.73 (K). Saffron and gamboge are organic pigments and they do not show any characterizing line. Yellow lake reseda (weld) exhibited a large Sn signal which could be indicative that a tin chloride mordant was used [37] (Fig. 8). Naples yellow, a lead antimonate, contains Pb and Sb with lines at 26.24 (K) and 29.73 (K). Massicot (lead (II) oxide) features Pb lines while

chrome yellow, a lead chromate, also features Cr lines. Cobalt yellow (potassium cobalt nitrite) and cadmium yellow (cadmium zinc sulfide) were dominated by Co and Cd, respectively. Finally, yellow ochre is unique to the yellows pigments featuring only Fe lines.

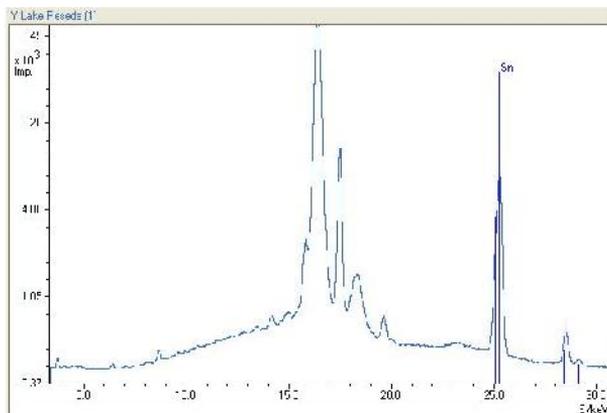


Fig. 8. XRF spectrum of yellow lake reseda showing Sn lines.

Conclusions

The XRF analysis of the 58 pigments is in agreement with the information provided by the pigments' manufacturers. Each of the pigments had XRF spectra consistent with the expected elemental content reported in literature. Further analysis with Raman, FT-IR and XRD will be pursued in order to expand our characterization of the pigments beyond the XRF elemental characterization. Pigments Checker is already used in a number of research projects and we wish that this contribution of a free and downloadable XRF spectral database will increase the implementation of Pigments Checker in other research and educational projects as a standard tool in Conservation Science.

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