



Microanalytical characterization of decorations in handmade ancient floor tiles using inductively coupled plasma optical emission spectrometry (ICP-OES)

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ABSTRACT

In this study a total of 114 glazed decorations of 42 ceramic floor tiles, manufactured in Sicily from the 16th to the 21th AD, were investigated. The micro sampling method, proposed by us, using a cotton swab soaked in hydrofluoric acid, includes advantages of high sensitivity, high selectivity, simplicity, speed, not expensive and can be considered non-destructive because the point of sampling remains invisible to the human eye. ICP-OES technique was used in this study. Twenty-four elements (Al, As, B, Be, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, Pb, Sb, Se, Si, Sn, Ti, V and Zn) were determined in each colored enamel.

Enameled decorations in Sicilian tiles were varied in tones and chromatic effects, obtained with a limited number compounds of cobalt, copper, iron, manganese, tin, and in the artifacts following the year 1920, also titanium. An important remark is that some of the colors, such as black, orange, purple and brown were prepared using the same metals, while white, light blue, blue and green were obtained with different elements. The adoption of different recipes for the same color suggests the presence of several laboratories of ceramists working in Sicily who had preferences for different methods for the production of their enameled artifacts.

Concerning the opacifier, the high amounts of lead and antimony, only in a case, indicate the use of lead antimonate ($\text{Pb}_2\text{Sb}_2\text{O}_7$). Black decorations were present in several of the analyzed samples and in most of them were identified mixtures of black iron and manganese oxides. The green decorations appear to have been prepared with copper oxide; lighter hue samples contained additional amounts of zinc and/or barium compounds. Considering all the samples, meanly, iron predominates in yellow decorations, only a sample contains large amounts of Cd, Zn and very little Sb, which suggests the use of the pigments ZnO (as white) and CdS as cadmium yellow. For all samples, except one, we can exclude the use of pigments containing chromium.

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1. Introduction

The application of analytical techniques to the study of historical and cultural heritage has led to a significant progress in the knowledge of human civilizations [1–4]. They also allow us to distinguish between objects which may have a similar visual appearance, but which were made using different raw materials or technological procedures [5–7].

Production of ceramic objects began in Sicily during prehistory and nonstop through the Roman and Medieval periods and still is active today [8]. Reasons for this well-known tile production in Sicily are associated with the presence of widespread utilizable clay deposits and, all at once, to the high level of expertise of local ceramists which has developed over the centuries [8]. The most important manufacturing areas, located in the central-eastern part of Sicily (Gela, Syracuse and Caltagirone), were strongly influenced by decorative motifs of Arabian

inspiration [8]. Starting from the 16th century, the production of Sicilian ceramic was expanded with the laboratories of Palermo, Sciacca, Burgio, Collesano and Naso. At the end of the 18th century, the pottery production of western Sicily decreased and, in the same period, a new production took place at Santo Stefano di Camastra, on the Tyrrhenian coast of eastern Sicily [8].

The chronological/spatial positioning of a given tile is generally definite by an expert art historian, whose evaluation is based on the style of decorations and on the association of colors and decorative motifs. Only in recent times, a systematic scientific study (archeometry) of Sicilian pottery has been carried out, aiming at a rational classification of local productions, namely understanding of manufacturing techniques and characterizing the composition of the raw materials [7,8].

The decorated ceramic floor tiles are a typical handicraft production. The feature of this kind of artifact is a whitish opaque or shiny glassy coating, usually obtained with white compounds (calcium antimonate, tin dioxide, lead carbonate, etc.) as a substrate for the pigments. Moreover, these objects are usually characterized by contrasting intense and bridge colors. Colors, generally, were obtained

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through metal oxides or synthesized pigments, for example Naples Yellow ($\text{Pb}_3(\text{SbO}_3)_2$), which were used singly or mixed with other pigments. In some cases, the compounds which make the surface opaque, also impart color to the background, for example, copper or copper (I) oxide in red opaque enamel or lead antimonite in yellow ones. The most common pigments present in ancient tiles contain metal ions, such as Cu(II), Fe(II), Fe(III), Mn(III), Mn(IV) and Co(II) dissolved in the enamel matrix.

The investigation of ancient ceramic technology, which was usually based on the analysis of the ceramic body [7] in the past, can be complemented through the analysis of the pigments used for surface decoration. Despite the importance of the craft ceramics, relatively few scientific studies concerning its pigments have been published [4,8,9]. The pigments are among the most interesting matrices to be investigated, because ancient people used many kinds of substances naturally or artificially. The metal identification in the pigments used in ancient works of art is important from the archeometry [10,11] and art history points of view, as well as for the restoration and reproduction of the artifacts.

The problem of pigment identification in ceramics could be resolved by the use of analytical techniques [9–12] some of them require big amounts of samples. The requirement of archeologists and curators for the use of non- or low destructive analytical techniques, during the examination of ancient material, makes inductively coupled plasma optical emission spectrometry (ICP-OES) technique an important tool for the analysis of the cultural heritage. Inductively coupled plasma emission spectrometry is one of the most important multi-elemental quantitative analytical techniques for the study of samples in environmental and cultural heritage sciences [7,13,14].

The present work is aimed to the investigation of ancient and recent ceramic floor tiles, coming from the Sicilian area (Southern Italy), in order to get information about the pigments used to produce the decorations, as a first step to understand the production technology of the Sicilian tile manufacturers. The identification of pigments used in tiles and potteries is important for their reproduction, restoration, dating, and authentication, as well as for obtaining artistic, technical and economic information.

In the present work, we report and discuss the experimental results obtained through ICP-OES measurements performed on a set of forty-two shards of ceramic tiles. In particular, in our case, the sampling procedure involved gently contacting a cotton swab soaked in HF with the decorated enameled surface to chemically remove an infinitesimal quantity of material that does not cause any visible effect to the object.

2. Experimental

2.1. Laboratory equipment

All glassware and sample containers were thoroughly washed with HNO_3 2% solution followed by rinsing with purified water. These were finally kept in the oven at 110 °C over night. To avoid contaminations of samples, different glassware and pipettes were used for standards and for solutions obtained from samples.

2.2. Samples

A set of 42 fragments of glazed ceramic floor tiles (Table 1), manufactured in Sicily in different times from the 16th to the 21th AD was studied. The choice of samples comprised several of the color motifs available among the great diversity of decorations found in ceramic floor tiles in different periods and production workshops. Fig. 1 shows some samples where the representative colors are depicted. Table 1 includes a full list of the analyzed samples, with the colors analyzed.

Table 1
List of samples analyzed and the identified colors.

Sample	Identified colors
1a	White–yellow–light blue–green–brown
1b	Green–yellow–brown–light blue
1bb	Brown
2a	Black–white–blue
5a	Yellow–brown
7a	Green–black
8a	White–green–brown
9a	White–blue
15a	Red–black
18a	Blue–white–black
20a	White–black
30n	Black
31n	Light blue
32n	Yellow–green–blue–light blue
33a	White
33n	Yellow–green–blue–white
34n	Light blue–white–orange–blue
35a	Blue
35n	White–light blue
36n	White–light blue
37a	White–blue–brown–light blue
38a	White–blue
39a	White
40a	Blue–white
41a	White–black–blue
44a	Brown
47a	White
48a	Green–light blue–brown–white
49a	Light yellow–brown
50a	White–green
51a	Blue–black–white
52a	Blue–white–brown–green–dark brown
53a	White–blue–black
54a	Blue–light blue
55a	White–blue–black
57a	White–light blue–pink–black
58a	White–yellow–red–light blue
bl	Brown
blar	Yellow–white–blue–green
magr	White–brown
mapi	White–brown
vec	Brown–white–green–light blue–light green–dark green–gray

Each analyzed sample was identified by one or two letters and an initial (for example b/9a) the first one indicating the color (a = orange, b = white, bl = blue, c = light blue, m = brown, n = black, p = pink, pu = purple), the second one the name of the sample.

The samples were provided by the markets of antiques (flea market) in Palermo and a few samples came from private collections.

2.3. Sampling

To obtain a sample of composition as representative as possible of the decorations, the following precautions were taken: a) the areas for analysis were selected where a layer of colored enamel was deposited and as far as possible from other colors; b) each decoration of the same color was analyzed in three different points of the same tile to verify the reliability of the sampling method (Fig. 2).

The sampling technique, proposed by us, involved gently contacting a cotton swab soaked in hydrofluoric acid (Riedel-de Haen, Trace Select, 40% v/v) with the decorated surface to chemically remove an extremely small quantity of pigment. The surface area sampled by the cotton can vary, depending on the amount of enamel that is removed. Usually about 0.20 cm² is contacted with the cotton swab. The amount of material removed from the ceramic surface is invisible to the eye and does not cause any visible effect to the artifact. The cotton swab was then placed in a 2 mL test tube containing HNO_3 (2% v/v). The solution transferred into a small PTFE beaker was placed on a hotplate and heated to dryness. The final residue was dissolved in 1.5 mL of HNO_3 (trace select



Fig. 1. Some of the studied floor tiles.

ultra for trace analysis 65%) and the final volume was adjusted using Millipore water prior to analysis using Inductively Coupled Plasma-Optical Emission Spectrometry.

2.4. ICP-OES analysis

Elemental analyses were carried out on the solutions obtained from the treatment of the samples using a Perkin Elmer Optima 2100 series ICP optical emission spectrometer. The instrument is equipped with a Perkin S10 model autosampler. Data acquisition and processing were performed using the Win Lab 32 software (Perkin Elmer). Operating conditions are listed in Table 2. Twenty-four elements (Al, As, B, Be,

Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, Pb, Sb, Se, Si, Sn, Ti, V and Zn) were determined in each sample, chosen on the basis of their significance in the study of pigments.

The ICP-OES analysis of trace elements was performed in axial viewing mode while those of major elements (Si, Al, K, Ca and Pb) in radial viewing mode. The quantitative analysis was performed at two different spectral lines for each element (Table 3). The data of the metals reported in this paper have been calculated considering the average of the values obtained at the two wavelengths that, for all analytes, differed by less than 5%. A total of 114 decorations were analyzed by about 3000 determinations of single elements.

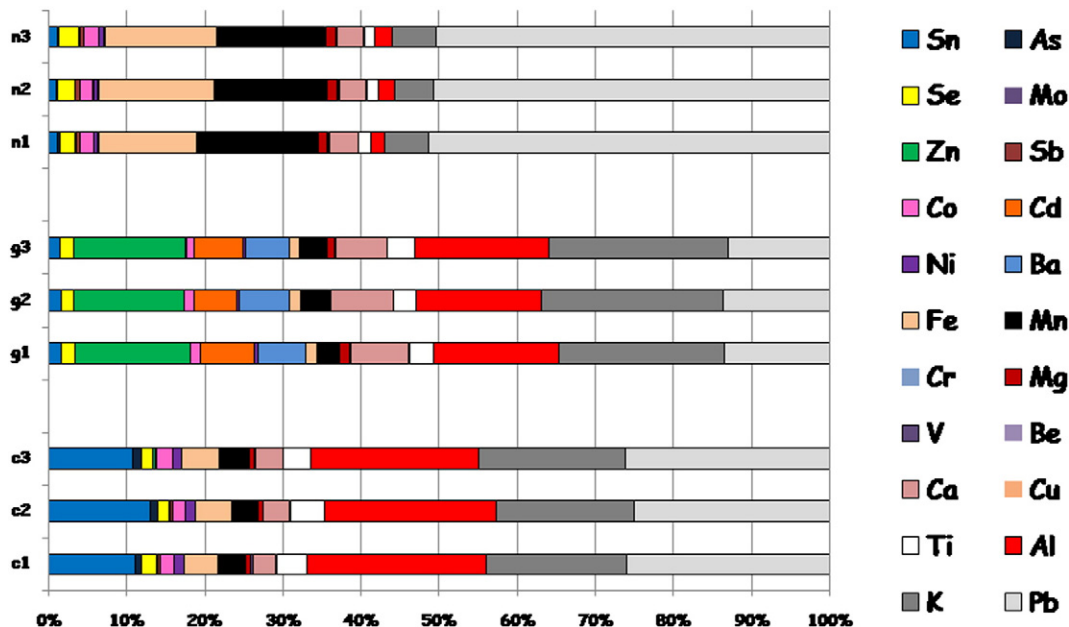


Fig. 2. Reproducibility of the sampling method.

Table 2
ICP-OES operating conditions.

RF power (W)	1300
Sample uptake flow rate (mL/min)	1.5
Gas flow rates (L/min)	Auxiliary: 0.2; Nebulizer: 0.8; Argon: 15
Viewing mode	Axial; radial

2.5. Calibration curves

The detection limit (LOD) and the quantification limit (LOQ) were estimated as reported in previous papers [7,15] and respectively ranged from 2 to 8 µg/L and from 6.6 to 25 µg/L. Calibration standard solutions were prepared by dilution with HNO₃ 2% of a multi-element calibration standard solution (Ultra Scientific, USA, catalog number: IQC-026, Lot n° J00022) that contained 26 elements. The range of concentration of the calibration curves was between 10 and 50,000 µg/L. For calibration, a solution of HNO₃ 2% as blank was used. The analysis of the six standard solutions was replicated in every eight samples. Correlation coefficients of the calibration curves were in the range of 0.9985–0.9999. To eliminate memory effects related to the previous sample analysis, between two subsequent samples, a 25 s washing was settled. A blank was run up every eight samples. All reported data were blank corrected.

3. Results and discussion

To evaluate the precision of the method and in particular the feasibility of using a cotton swab for sampling glazed decorations, three replicates, sampled in different points of the same decorations (light blue c1–c3, yellow g1–g3, black n1–n3) were analyzed (Fig. 2). The relative standard deviations of the replicates on the concentrations of major metals ranged from 1% to 8% and are satisfactory for the purpose of this work.

The accuracy of analytical method was valued by analyzing samples prepared by us spiked with known amounts of some elements to solutions obtained from four samples. The recovery percentage ranged between 92% and 101%.

Silicon is the most abundant element in all the samples and so its concentration cannot be useful to distinguish samples. Considering

Table 3
Wavelengths used for elemental determinations by ICP-OES.

Element	Wavelength 1 (nm)	Wavelength 2 (nm)
Al	396.153	308.215
As	193.696	188.979
B	249.677	249.772
Ba	233.527	455.403
Be	313.107	313.042
Ca	317.933	315.887
Cd	228.802	214.440
Co	228.616	238.892
Cr	267.716	205.560
Cu	327.393	324.752
Fe	238.204	239.562
K	766.490	404.721
Mg	285.213	279.077
Mn	257.610	259.372
Mo	202.031	203.845
Ni	231.604	221.648
Pb	220.353	217.000
Sb	206.836	217.582
Se	196.026	203.985
Si	251.611	212.412
Sn	189.927	235.485
Ti	334.490	336.121
V	292.464	310.230
Zn	206.200	213.857

that the sampling procedure is not quantitative, to discuss and interpret the data, we normalized the concentration of the single metal, measured in the solution obtained from the sample, to that of silicon, determined within the same sampling point. Results (mean of three sampling) of chemical elemental ICP-OES analyses of the sampled material are reported in Table 4(a–i). All samples are mainly composed of Si, Pb, Al and K. Pb/Si and Al/Si ratios, for different samples, ranged respectively from 0.114 (yellow) to 3.69 (pink) and from 0.004 (pink) to 0.160 (light blue). The relatively high amount of aluminum points to the employment of alumina silicates in vitreous coatings, in fact Al/Si is, except for light blue and pink decorations, practically constant in all the colors (Fig. 3). In general, the presence of lead is compatible with the addition of a lead–tin calx to colorless enamels. The different lead to tin ratios (from 4.3 to 29.7) were probably related to the control of the viscosity and opacity of the enamels.

Also other elements, such as beryllium, boron and vanadium, have been quantified, but these have not been included in the discussion, because they did not contribute to the pigment individuation.

From the collected data, in general, we can deduce that most of the decorations associated to one color had a similar elemental composition and that the different colors could be associated with different coloring elements. In Fig. 4 the relation between the percentages of the metals and the colors of the decorations is shown.

Considering all the analyzed samples, copper is present in higher amounts in green decorations. Iron is present in higher percentages in the black, brown and yellow decorations. High amounts of Ca, Zn, Sb, Ti and Pb were found mainly in pastel enamels.

The white decorations of all the tiles, except three samples (b/33n, b/58a and b/52a), contained large amounts of Pb (Pb/Si = 0.38), Sn (Sn/Si = 0.086) and Al (Al/Si = 0.086) and very little other elements (Fig. 5) which suggest the use of the pigments 2PbCO₃·Pb(OH)₂ (lead white) and SnO₂ (cassiterite). These compounds were used directly by themselves or mixed with other colored pigments in order to obtain different tonalities. The ratio of lead to tin in the studied tiles varies from about zero (b/33n, b/52a) to nearly 30 (b/36n). The use of different lead to tin ratios was probably related to the control of the opacity of the white areas. It should be noticed that sample b/58a showed Zn as metal. The white zinc pigments appeared for the first time in England in 1834 [16]. The presence of this pigment in this sample indicates a decoration layer from at least the 19th century.

The presence of higher concentrations of tin (Sn/Si = 1.61) only in sample b/33n than other white samples can be an indicator that the pigment used in this area was the compound SnO₂. The presence of large concentrations of titanium (Ti/Si = 0.14) only in sample b/52a can be an indicator that the pigment used in these areas was the compound TiO₂ (titanium dioxide white), while in all other samples, the Ti/Si ratios are similar to that of the crust Ti (Ti/Si = 0.023) [17]. The deliberate use of TiO₂ as ancient pigment has not been known [18,19], its first use in objects of art came only after industrial processes were developed in the first years of 1900 for producing a pure and brilliant white. The presence of this pigment in the sample b/52a indicates a decoration from at least the 20th century. Other white pigments were not used such as lead arsenate (since the 17th century, a more effective opacifier).

The yellow decorations, mainly, contained large amounts of Pb (Pb/Si = 0.11), Al (Al/Si = 0.090), Sn (Sn/Si = 0.027), Fe (Fe/Si = 0.023) and very little other elements (Fig. 6), which suggests the use of lead and iron based pigments. We can suppose that the yellow enamels are made mainly of lead and iron oxides (PbO, Fe₂O₃, etc.). A significant difference concerns sample g/58a contained large amounts of Cd (Cd/Si = 0.043) which suggests the use of the pigments CdS.

The presence of antimony in a yellow decoration (g/33n) is consistent with the use of Naples Yellow (Pb₂Sb₂O₇). Some studies

Table 4
Chemical composition (normalized to silicon) of the colored decorations determined by ICP-OES.

a														
	b/gr	b/9a	b/1a	b/ve	b/blar	b/34n	b/8a	b/mp	b/mg	b/20a	b/2a	b/33n	b/35n	b/47a
Al	0.047	0.14	0.047	0.11	0.12	0.059	0.16	0.10	0.12	0.097	0.14	0.096	0.049	0.074
As	0.0006	0.0007	0.0001	0.001	0.0012	0.0008	0.0007	0.0007	0.0009	0.0006	0.0007	0.0024	0.001	0.0014
Ba	0.0002	0.0002	0.0019	0.0003	0.0037	0.0052	0.0003	0.0002	0.0002	0.0002	0.0002	0.018	0.0009	0.001
Be	0.0001	0.0001	0.0001	0.0002	0.0001	0.0001	0.0002	0.0001	0.0001	0.0001	0.0001	0.0002	0.0002	0.0004
Ca	0.010	0.0056	0.0095	0.0064	0.016	0.012	0.0026	0.0053	0.012	0.0027	0.0061	0.023	0.0014	0.015
Cd	0.0001	0.0001	0.0028	0.0001	0.0018	0.002	0.0001	0.0001	0.0001	0.0001	0.0001	0.0005	0.0002	0.0003
Co	0.0037	0.0034	0.0052	0.0064	0.0081	0.0097	0.0049	0.0040	0.0039	0.0046	0.0045	0.024	0.012	0.014
Cr	0.0001	0.0001	0.0007	0.0001	0.001	0.0012	0.0001	0.0001	0.0001	0.0001	0.0001	0.0036	0.0002	0.0002
Cu	0.0004	0.0003	0.0023	0.0011	0.0013	0.0013	0.0004	0.0003	0.0003	0.0003	0.0003	0.0036	0.0004	0.0002
Fe	0.007	0.0076	0.0064	0.0077	0.012	0.0058	0.013	0.0074	0.010	0.012	0.0039	0.0088	0.0086	0.016
K	0.036	0.090	0.069	0.042	0.069	0.061	0.064	0.055	0.058	0.024	0.036	0.054	0.021	0.078
Mg	0.0029	0.0021	0.0037	0.0011	0.0053	0.0069	0.0027	0.0021	0.003	0.0018	0.0013	0.025	0.0028	0.006
Mn	0.0094	0.0008	0.013	0.0304	0.019	0.021	0.0005	0.0099	0.0098	0.012	0.011	0.057	0.027	0.034
Mo	0.0021	0.0038	0.003	0.0002	0.0053	0.0052	0.0006	0.0001	0.0001	0.0002	0.0001	0.0011	0.0005	0.0004
Ni	0.002	0.0016	0.003	0.0019	0.0044	0.005	0.0016	0.0013	0.0013	0.0015	0.0014	0.0137	0.0038	0.0045
Pb	0.13	0.070	0.14	0.067	0.21	0.12	0.25	0.31	0.50	0.33	0.32	0.01	0.43	0.54
Sb	0.0011	0.0009	0.0017	0.0016	0.0034	0.0027	0.0001	0.0003	0.0003	0.0002	0.0004	0.0088	0.0011	0.0009
Se	0.0044	0.0068	0.0063	0.0089	0.0095	0.011	0.0066	0.0053	0.0052	0.0061	0.0066	0.032	0.016	0.019
Sn	0.034	0.035	0.0091	0.030	0.034	0.053	0.017	0.026	0.028	0.028	0.032	1.61	0.033	0.055
Ti	0.0091	0.0051	0.0122	0.004	0.018	0.02	0.017	0.012	0.012	0.014	0.014	0.089	0.027	0.034
Zn	0.0004	0.0011	0.0025	0.0002	0.0043	0.026	0.0084	0.0002	0.0002	0.0038	0.0004	0.064	0.0031	0.0011
b														
	b/48a	b/38a	b/39a	b/40a	b/37a	b/36n	b/18a	b/50a	b/51a	b/58a	b/41a	b/ve	b/52a	gr/vec
Al	0.024	0.17	0.032	0.14	0.13	0.037	0.12	0.073	0.088	0.081	0.066	0.016	0.001	0.0001
As	0.0071	0.0006	0.001	0.0016	0.0008	0.0012	0.0017	0.0011	0.0008	0.0009	0.0006	0.0014	0.0001	0.060
Ba	0.0008	0.0002	0.0011	0.0003	0.0004	0.001	0.0009	0.0011	0.0005	0.025	0.0003	0.0009	0.0055	0.0076
Be	0.0003	0.0001	0.0003	0.0001	0.0002	0.0004	0.0004	0.0004	0.0003	0.0003	0.0002	0.0004	0.0021	0.0002
Ca	0.0276	0.0127	0.0256	0.0118	0.003	0.0066	0.0101	0.003	0.0055	0.045	0.0014	0.018	0.003	0.0001
Cd	0.0003	0.0001	0.0002	0.0001	0.0001	0.0003	0.0003	0.0002	0.0002	0.0061	0.0001	0.0001	0.0012	0.0015
Co	0.0108	0.0055	0.011	0.0049	0.0078	0.0335	0.0125	0.0109	0.0094	0.010	0.0057	0.012	0.066	0.020
Cr	0.0002	0.0001	0.0002	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002
Cu	0.0044	0.0003	0.0002	0.0007	0.0001	0.0002	0.0004	0.0026	0.0019	0.018	0.0002	0.0018	0.0001	0.0001
Fe	0.027	0.0059	0.0099	0.0069	0.0042	0.0105	0.0067	0.021	0.0061	0.0073	0.0043	0.020	0.0014	0.047
K	0.11	0.12	0.041	0.089	0.067	0.031	0.025	0.0713	0.0713	0.0573	0.040	0.059	0.001	0.066
Mg	0.0084	0.0021	0.0062	0.0024	0.0016	0.0023	0.0021	0.003	0.0021	0.0056	0.0015	0.0062	0.0011	0.0002
Mn	0.032	0.0008	0.0016	0.0013	0.0011	0.031	0.030	0.026	0.022	0.024	0.001	0.030	0.16	0.020
Mo	0.0003	0.0002	0.0004	0.0001	0.0003	0.0005	0.0004	0.0003	0.0003	0.0003	0.0002	0.0004	0.0022	0.0003
Ni	0.0038	0.0018	0.0037	0.0015	0.0025	0.0047	0.004	0.0035	0.0003	0.0033	0.0019	0.0040	0.021	0.0073
Pb	1.6	0.35	0.50	0.42	0.49	0.63	0.43	0.35	0.43	0.025	0.28	0.71	0.001	0.84
Sb	0.0012	0.0018	0.0008	0.0008	0.0007	0.0023	0.0009	0.0011	0.0032	0.0006	0.0004	0.0023	0.0053	0.0016
Se	0.014	0.0076	0.015	0.0062	0.011	0.017	0.017	0.015	0.013	0.014	0.008	0.017	0.12	0.0096
Sn	0.11	0.049	0.036	0.025	0.039	0.021	0.0267	0.039	0.041	0.044	0.029	0.051	0.042	0.026
Ti	0.025	0.0076	0.0023	0.0045	0.0054	0.029	0.0303	0.0255	0.0226	0.026	0.0028	0.029	0.14	0.016
Zn	0.0009	0.0011	0.0042	0.002	0.0025	0.047	0.0002	0.0002	0.0004	0.11	0.0004	0.0004	0.0001	0.0005
c														
	b/55a	b/33a	b/53a	b/57a	g/1a	g/1b	g/32n	g/33n	g/blar	g/58a	gc/49a	g/5a	a/34n	p/57a
Al	0.12	0.050	0.0439	0.083	0.09	0.0311	0.068	0.11	0.081	0.13	0.055	0.15	0.10	0.004
As	0.0007	0.0004	0.0007	0.0008	0.0009	0.0014	0.0022	0.0022	0.0032	0.0007	0.0008	0.0015	0.0045	0.015
Ba	0.0005	0.0004	0.0008	0.0009	0.0014	0.0027	0.018	0.0194	0.0008	0.0374	0.0009	0.0022	0.026	0.008
Be	0.0002	0.0002	0.0003	0.0003	0.0002	0.0002	0.0005	0.0001	0.0001	0.0002	0.0003	0.0002	0.00075	0.004
Ca	0.0071	0.002	0.0051	0.003	0.012	0.0051	0.034	0.0309	0.0092	0.0459	0.0002	0.017	0.050	0.0001
Cd	0.0001	0.0001	0.0002	0.0002	0.0008	0.0017	0.0024	0.0072	0.002	0.0427	0.0003	0.0002	0.014	0.002
Co	0.0076	0.0066	0.0001	0.0119	0.0033	0.0073	0.0171	0.023	0.009	0.0076	0.012	0.0066	0.068	0.151
Cr	0.0002	0.0001	0.0001	0.0001	0.0001	0.0009	0.0002	0.0026	0.0011	0.0001	0.0001	0.0001	0.0079	0.0001
Cu	0.0002	0.0002	0.0002	0.0001	0.0092	0.0041	0.0009	0.0022	0.0016	0.0004	0.0001	0.0008	0.0060	0.0001
Fe	0.0274	0.0074	0.01	0.015	0.026	0.014	0.0065	0.011	0.060	0.0092	0.037	0.024	0.041	0.005
K	0.053	0.047	0.037	0.041	0.072	0.062	0.037	0.032	0.053	0.083	0.038	0.047	0.0092	0.40
Mg	0.003	0.0019	0.0034	0.0027	0.0035	0.004	0.0046	0.013	0.0049	0.0074	0.0013	0.0033	0.00019	0.0001
Mn	0.0183	0.016	0.027	0.0291	0.0123	0.018	0.0022	0.044	0.021	0.018	0.0022	0.0022	0.14	0.33
Mo	0.0002	0.0003	0.0004	0.0004	0.0021	0.0042	0.0006	0.011	0.005	0.0002	0.0003	0.0003	0.034	0.004
Ni	0.0025	0.0021	0.0041	0.0038	0.0021	0.0041	0.0054	0.011	0.0049	0.0024	0.0038	0.0021	0.033	0.046
Pb	0.73	0.42	0.39	0.47	0.15	0.091	0.089	0.079	0.068	0.10	0.24	0.092	0.28	3.7
Sb	0.0006	0.0007	0.0011	0.0008	0.0052	0.0068	0.0047	0.030	0.0043	0.0006	0.0007	0.0097	0.082	0.01
Se	0.010	0.0091	0.015	0.020	0.0048	0.0089	0.024	0.024	0.01	0.011	0.016	0.0091	0.074	0.19
Sn	0.022	0.030	0.023	0.0247	0.0323	0.045	0.027	0.035	0.017	0.01	0.0155	0.030	0.036	0.407
Ti	0.021	0.016	0.026	0.0288	0.0106	0.016	0.026	0.086	0.019	0.0194	0.003	0.022	0.12	0.292
Zn	0.0006	0.0003	0.0027	0.0003	0.0025	0.0026	0.031	0.070	0.0042	0.091	0.0029	0.001	0.11	0.002

(continued on next page)

Table 4 (continued)

d														
	r/15a	r/58a	c/ver	c/34n	c/1a	c/31n	c/32n	c/48a	c/37a	c/36n	c/54a	c/1b	c/58a	c/35n
Al	0.023	0.12	1.14	0.12	0.034	0.088	0.074	0.012	0.15	0.047	0.10	0.087	0.086	0.050
As	0.0011	0.0033	0.020	0.0017	0.004	0.0016	0.0014	0.078	0.0015	0.0009	0.0007	0.0033	0.0007	0.001
Ba	0.0003	0.044	0.0009	0.0153	0.0023	0.0026	0.0085	0.0068	0.0011	0.0011	0.0027	0.0001	0.0286	0.001
Be	0.0003	0.0002	0.0007	0.0003	0.0001	0.0002	0.0004	0.0003	0.0004	0.0004	0.0003	0.0002	0.0002	0.0004
Ca	0.0093	0.033	0.0651	0.0994	0.0083	0.054	0.011	0.0083	0.014	0.0001	0.0079	0.0108	0.0595	0.0001
Cd	0.0002	0.0658	0.0004	0.0048	0.0014	0.0002	0.0004	0.0018	0.0003	0.0003	0.0002	0.0001	0.0073	0.0003
Co	0.0091	0.006	0.0409	0.0351	0.0075	0.020	0.0174	0.0209	0.022	0.017	0.012	0.0068	0.0069	0.0153
Cr	0.032	0.0001	0.0008	0.0028	0.0008	0.0001	0.0002	0.0002	0.0002	0.0001	0.0001	0.0001	0.0002	0.0001
Cu	0.0026	0.0018	0.0043	0.0021	0.010	0.0002	0.0034	0.0035	0.0001	0.0002	0.0003	0.0007	0.085	0.0005
Fe	0.0124	0.0092	0.065	0.0099	0.0081	0.0066	0.0069	0.025	0.0080	0.0058	0.0103	0.0164	0.0072	0.0062
K	0.0228	0.0744	0.54	0.044	0.068	0.051	0.040	0.065	0.080	0.036	0.071	0.069	0.075	0.027
Mg	0.0044	0.0068	0.018	0.022	0.0038	0.0061	0.0039	0.0056	0.0039	0.0021	0.0028	0.0027	0.0065	0.0023
Mn	0.0023	0.0144	0.064	0.048	0.015	0.0008	0.029	0.030	0.005	0.034	0.024	0.0131	0.016	0.032
Mo	0.0003	0.0002	0.0007	0.0121	0.0035	0.0002	0.0004	0.0004	0.0005	0.0006	0.0003	0.0001	0.0002	0.0005
Ni	0.0029	0.0019	0.015	0.0117	0.0059	0.0022	0.0041	0.0085	0.0053	0.0047	0.0031	0.0048	0.0023	0.0044
Pb	0.063	0.15	0.22	0.26	0.11	0.25	0.23	0.57	0.71	0.28	0.45	0.098	0.023	0.25
Sb	0.0013	0.0004	0.0064	0.0062	0.0021	0.0004	0.0009	0.0012	0.0013	0.0013	0.0014	0.0009	0.0004	0.0014
Se	0.012	0.0104	0.029	0.026	0.0073	0.0093	0.0184	0.0158	0.0216	0.020	0.013	0.0072	0.0095	0.019
Sn	0.065	0.0052	0.32	0.0001	0.045	0.001	0.020	0.043	0.0349	0.030	0.025	0.042	0.043	0.027
Ti	0.014	0.016	0.076	0.044	0.014	0.0037	0.017	0.026	0.0055	0.033	0.023	0.015	0.021	0.0314
Zn	0.0009	0.0936	0.0036	0.15	0.010	0.072	0.048	0.0008	0.0079	0.0068	0.0041	0.0008	0.14	0.0048
e														
	c/57a	v/ve	v/1a	v/1b	v/7a	v/8a	v/blar	v/33n	v/32n	v/52a	v/50a	v/48a	vc/vec	vs/vec
Al	0.10	0.090	0.096	0.075	0.14	0.14	0.072	0.047	0.054	0.080	0.053	0.023	0.053	0.033
As	0.0025	0.004	0.0007	0.0002	0.0013	0.0005	0.0052	0.0013	0.0013	0.0026	0.0013	0.002	0.0036	0.0352
Ba	0.0014	0.0023	0.001	0.0028	0.003	0.006	0.0008	0.0153	0.0186	0.0012	0.0009	0.0007	0.001	0.0143
Be	0.0006	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002	0.0001	0.0003	0.0005	0.0002	0.0003	0.0004	0.0004
Ca	0.0053	0.0079	0.025	0.0067	0.0153	0.0074	0.019	0.030	0.0445	0.0049	0.0111	0.016	0.028	0.0491
Cd	0.0004	0.0001	0.0006	0.0017	0.0018	0.0001	0.0024	0.0036	0.0009	0.0003	0.0001	0.0002	0.0003	0.0013
Co	0.0235	0.0069	0.0027	0.0077	0.0079	0.0082	0.012	0.016	0.012	0.017	0.0082	0.0114	0.013	0.030
Cr	0.0002	0.0001	0.0001	0.0012	0.0011	0.0009	0.0037	0.0021	0.0002	0.0001	0.0001	0.0002	0.0002	0.0002
Cu	0.0001	0.0165	0.039	0.059	0.038	0.0049	0.0036	0.23	0.14	0.023	0.050	0.037	0.049	0.020
Fe	0.013	0.0164	0.022	0.022	0.0105	0.012	0.022	0.028	0.0049	0.013	0.024	0.026	0.062	0.0123
K	0.04	0.050	0.084	0.059	0.046	0.047	0.12	0.020	0.032	0.041	0.079	0.062	0.078	0.099
Mg	0.0046	0.002	0.0051	0.0066	0.0062	0.0027	0.0079	0.01	0.0053	0.0029	0.0041	0.0062	0.0094	0.019
Mn	0.046	0.013	0.0069	0.018	0.019	0.0085	0.025	0.037	0.0039	0.043	0.032	0.033	0.032	0.0391
Mo	0.0006	0.0001	0.0016	0.0044	0.0046	0.0002	0.0003	0.0091	0.0004	0.0005	0.0002	0.0003	0.0002	0.0005
Ni	0.0064	0.0027	0.0016	0.0045	0.0053	0.0011	0.0034	0.009	0.0039	0.0051	0.0026	0.0038	0.0042	0.01
Pb	0.76	0.063	0.33	0.16	0.19	0.59	0.099	0.0049	0.015	0.50	0.38	1.1	0.52	1.1
Sb	0.0015	0.0078	0.0012	0.0033	0.0035	0.0056	0.0063	0.0048	0.0016	0.0028	0.0023	0.001	0.0034	0.0079
Se	0.027	0.0051	0.0036	0.0093	0.0094	0.0045	0.012	0.021	0.017	0.022	0.011	0.0167	0.016	0.019
Sn	0.0346	0.035	0.0091	0.021	0.043	0.019	0.27	0.034	0.030	0.17	0.036	0.079	0.051	0.066
Ti	0.045	0.011	0.0095	0.019	0.0204	0.013	0.021	0.085	0.044	0.036	0.0193	0.027	0.038	0.037
Zn	0.0001	0.0013	0.0014	0.005	0.006	0.0026	0.0064	0.051	0.035	0.0005	0.0014	0.0004	0.0016	0.0017
f														
	bl/2a	bl/32n	bl/35n	bl/18a	bl/33n	bl/40a	bl/51a	bl/41a	bl/9a	bl/blar	bl/34n	bl/37a	bl/38a	bl/54a
Al	0.093	0.056	0.032	0.15	0.061	0.083	0.055	0.001	0.15	0.11	0.0057	0.12	0.18	0.075
As	0.0008	0.0016	0.0008	0.0077	0.0016	0.0066	0.003	0.0051	0.0005	0.0097	0.0003	0.0008	0.0005	0.0009
Ba	0.0024	0.014	0.0009	0.0003	0.018	0.0021	0.0004	0.004	0.0002	0.001	0.0015	0.0006	0.0004	0.0041
Be	0.0001	0.0001	0.0003	0.0002	0.0001	0.0004	0.0002	0.0018	0.0001	0.0001	0.0001	0.0003	0.0001	0.0002
Ca	0.031	0.031	0.0035	0.0096	0.024	0.018	0.0051	0.0003	0.0044	0.010	0.003	0.0023	0.011	0.015
Cd	0.0001	0.0004	0.0003	0.0003	0.0055	0.0004	0.0001	0.0012	0.0052	0.0008	0.0008	0.0002	0.0001	0.0001
Co	0.0354	0.0323	0.0233	0.023	0.070	0.032	0.017	0.17	0.0202	0.022	0.0086	0.032	0.022	0.0236
Cr	0.0001	0.0002	0.0001	0.0001	0.0031	0.0002	0.0001	0.001	0.0001	0.0001	0.0005	0.0001	0.0001	0.0001
Cu	0.0007	0.0019	0.0003	0.0007	0.0032	0.0011	0.0031	0.0002	0.0004	0.0009	0.0004	0.0002	0.0002	0.0004
Fe	0.0097	0.0106	0.009	0.011	0.0067	0.0107	0.0077	0.0006	0.0091	0.015	0.0011	0.004	0.0061	0.012
K	0.047	0.041	0.024	0.044	0.055	0.076	0.045	0.14	0.068	0.062	0.013	0.055	0.088	0.061
Mg	0.0043	0.0054	0.0025	0.0027	0.0143	0.005	0.0025	0.001	0.0018	0.0032	0.0022	0.0013	0.0022	0.0027
Mn	0.0113	0.032	0.029	0.015	0.056	0.0024	0.017	0.0059	0.0011	0.0066	0.0084	0.0013	0.0007	0.015
Mo	0.0001	0.0082	0.0005	0.0003	0.0141	0.0004	0.0002	0.002	0.0001	0.0001	0.0021	0.0003	0.0001	0.0001
Ni	0.0027	0.0079	0.0043	0.0025	0.014	0.0054	0.0029	0.018	0.0014	0.0032	0.002	0.004	0.0015	0.0024
Pb	0.37	0.031	0.32	0.54	0.026	0.71	0.39	1.7	0.055	0.14	0.015	0.43	0.59	0.43
Sb	0.0009	0.001	0.0018	0.0008	0.0076	0.0019	0.0057	0.0063	0.0006	0.0014	0.0011	0.0008	0.0012	0.0015
Se	0.0061	0.0187	0.017	0.008	0.032	0.019	0.0092	0.077	0.0053	0.0034	0.0045	0.013	0.0064	0.0081
Sn	0.037	0.033	0.020	0.025	0.040	0.018	0.034	0.12	0.019	0.0265	0.0067	0.025	0.0236	0.027
Ti	0.013	0.0466	0.028	0.016	0.11	0.0029	0.017	0.0006	0.0057	0.0091	0.0074	0.0061	0.0074	0.036
Zn	0.0072	0.078	0.025	0.0003	0.16	0.0001	0.0003	0.094	0.0013	0.0025	0.0091	0.050	0.0004	0.030
g														
	bl/53a	bl/52a	bl/55a	bl/35a	m/1b	m/1bb	m/1a	m/bl	m/5a	m/ve	m/8a	m/map	m/44a	m/mgr
Al	0.044	0.06	0.12	0.033	0.087	0.11	0.078	0.13	0.11	0.062	0.12	0.069	0.11	0.059

Table 4 (continued)

g														
	bl/53a	bl/52a	bl/55a	bl/35a	m/1b	m/1bb	m/1a	m/bl	m/5a	m/ve	m/8a	m/map	m/44a	m/mgr
As	0.0007	0.013	0.0005	0.019	0.0009	0.0016	0.0009	0.0015	0.0013	0.0011	0.0018	0.0026	0.0014	0.0063
Ba	0.0008	0.0006	0.0004	0.0083	0.0001	0.0005	0.0017	0.0019	0.0005	0.0003	0.0084	0.0005	0.0011	0.0026
Be	0.0003	0.0002	0.0001	0.0009	0.0001	0.0003	0.0001	0.0004	0.0002	0.0001	0.0003	0.0004	0.0004	0.0005
Ca	0.0051	0.0038	0.0031	0.0051	0.005	0.0067	0.0084	0.0128	0.0083	0.012	0.011	0.0028	0.014	0.0102
Cd	0.0002	0.0004	0.0001	0.0007	0.0001	0.0002	0.0029	0.0004	0.0002	0.0001	0.0056	0.0001	0.0006	0.0003
Co	0.0001	0.0257	0.0221	0.061	0.004	0.0087	0.0046	0.019	0.0062	0.0039	0.022	0.0052	0.0144	0.008
Cr	0.0001	0.0001	0.0002	0.0011	0.0001	0.0002	0.0001	0.0002	0.0001	0.0002	0.0026	0.0001	0.0002	0.0001
Cu	0.0002	0.0018	0.0002	0.0006	0.0012	0.0011	0.0038	0.0004	0.0008	0.005	0.0002	0.0003	0.0099	0.0006
Fe	0.01	0.011	0.0182	0.0047	0.012	0.046	0.0085	0.013	0.015	0.022	0.033	0.049	0.054	0.10
K	0.037	0.11	0.045	0.017	0.065	0.056	0.0703	0.089	0.028	0.027	0.038	0.037	0.049	0.039
Mg	0.0034	0.0031	0.0025	0.0031	0.0022	0.002	0.0032	0.0024	0.0026	0.0039	0.0049	0.0026	0.0044	0.0028
Mn	0.027	0.021	0.012	0.078	0.086	0.036	0.078	0.057	0.074	0.30	0.051	0.013	0.058	0.083
Mo	0.0004	0.0064	0.0001	0.0009	0.0001	0.0002	0.0026	0.0007	0.0006	0.0001	0.013	0.0001	0.0004	0.0002
Ni	0.0041	0.0037	0.0021	0.010	0.0012	0.0027	0.0026	0.0046	0.002	0.0012	0.012	0.0017	0.0046	0.0025
Pb	0.39	0.33	0.28	0.021	0.0011	0.11	0.11	0.17	0.053	0.053	0.066	0.24	0.30	0.39
Sb	0.0011	0.0013	0.0003	0.0025	0.0006	0.0173	0.0021	0.0015	0.0046	0.0022	0.0065	0.0005	0.0034	0.0011
Se	0.015	0.012	0.0066	0.046	0.0055	0.0118	0.0055	0.018	0.009	0.0051	0.026	0.007	0.019	0.0093
Sn	0.023	0.023	0.013	0.055	0.0061	0.034	0.031	0.029	0.024	0.0164	0.0028	0.016	0.035	0.023
Ti	0.026	0.021	0.015	0.11	0.012	0.021	0.012	0.047	0.0054	0.011	0.047	0.014	0.034	0.021
Zn	0.0027	0.0004	0.0006	0.090	0.0013	0.0007	0.0021	0.0006	0.0005	0.0006	0.088	0.0007	0.001	0.0004
h														
	m/37a	m/48a	m/49a	m/52a	ms/52	n/15a	n/7a	n/20a	n/2a	n/30n	n/41a	n/51a	n/18a	n/57a
Al	0.083	0.017	0.025	0.057	0.074	0.053	0.072	0.050	0.11	0.018	0.015	0.068	0.16	0.029
As	0.0015	0.003	0.0015	0.0024	0.0025	0.0031	0.0034	0.0008	0.0009	0.0019	0.0025	0.0006	0.0025	0.0012
Ba	0.0015	0.0006	0.0019	0.0018	0.0015	0.0012	0.0079	0.0023	0.0006	0.0016	0.0021	0.0017	0.0008	0.0011
Be	0.0005	0.0003	0.00061	0.0007	0.0006	0.0005	0.0003	0.0002	0.0002	0.0004	0.0007	0.0003	0.0003	0.0004
Ca	0.0004	0.012	0.00046	0.0019	0.0044	0.030	0.017	0.0001	0.012	0.031	0.0011	0.005	0.017	0.0004
Cd	0.0004	0.0003	0.00053	0.0005	0.0004	0.0004	0.0045	0.0001	0.0001	0.0003	0.0006	0.0001	0.0002	0.0002
Co	0.0188	0.011	0.021	0.022	0.020	0.02	0.020	0.0071	0.0083	0.015	0.024	0.0095	0.013	0.014
Cr	0.0001	0.0002	0.00015	0.0002	0.0001	0.013	0.0026	0.0001	0.0002	0.0002	0.0004	0.0001	0.0001	0.0000
Cu	0.0005	0.029	0.0001	0.0022	0.015	0.078	0.018	0.0002	0.0023	0.001	0.0002	0.0018	0.0007	0.0004
Fe	0.033	0.034	0.055	0.0132	0.0141	0.026	0.11	0.16	0.010	0.11	0.050	0.087	0.0113	0.051
K	0.056	0.077	0.018	0.0321	0.0361	0.021	0.011	0.014	0.028	0.049	0.018	0.057	0.033	0.029
Mg	0.0018	0.0061	0.0016	0.0032	0.0032	0.0067	0.011	0.0019	0.0036	0.011	0.0039	0.0032	0.0037	0.0006
Mn	0.002	0.065	0.065	0.083	0.078	0.0028	0.15	0.059	0.075	0.13	0.049	0.051	0.067	0.033
Mo	0.0006	0.0003	0.00061	0.0006	0.0006	0.0006	0.0004	0.0002	0.0002	0.0004	0.0008	0.0004	0.0003	0.0001
Ni	0.006	0.0006	0.0067	0.007	0.0063	0.0059	0.0112	0.0023	0.0023	0.0047	0.0079	0.003	0.0034	0.0045
Pb	0.24	0.94	0.13	0.37	0.42	0.048	0.17	0.35	0.49	0.45	0.29	0.24	0.90	0.47
Sb	0.0012	0.0011	0.0011	0.0022	0.003	0.0014	0.0074	0.0001	0.0006	0.004	0.0016	0.001	0.0012	0.0009
Se	0.026	0.014	0.029	0.030	0.027	0.027	0.022	0.0094	0.0094	0.018	0.033	0.012	0.025	0.018
Sn	0.014	0.086	0.026	0.031	0.030	0.099	0.054	0.020	0.031	0.010	0.017	0.027	0.026	0.023
Ti	0.0101	0.026	0.046	0.049	0.044	0.15	0.046	0.0165	0.0198	0.013	0.0014	0.022	0.026	0.029
Zn	0.085	0.0007	0.042	0.0008	0.0005	0.033	0.015	0.061	0.001	0.0009	0.0007	0.0005	0.0003	0.0007
i														
	n/51a				n/53a				n/55a					
Al	0.067				0.055				0.077					
As	0.0006				0.0008				0.0011					
Ba	0.0006				0.0009				0.01					
Be	0.0003				0.0004				0.0005					
Ca	0.073				0.0088				0.0013					
Cd	0.0001				0.0002				0.0003					
Co	0.0095				0.013				0.016					
Cr	0.0001				0.0002				0.0003					
Cu	0.0018				0.0003				0.0004					
Fe	0.087				0.037				0.069					
K	0.057				0.039				0.040					
Mg	0.0032				0.0035				0.0032					
Mn	0.051				0.034				0.037					
Mo	0.0004				0.0005				0.0005					
Ni	0.003				0.004				0.005					
Pb	0.24				0.51				0.26					
Sb	0.001				0.0036				0.0016					
Se	0.012				0.017				0.021					
Sn	0.026				0.027				0.020					
Ti	0.022				0.029				0.037					
Zn	0.0005				0.0008				0.0011					

regarding Naples Yellow have been published with particular attention given to the identification of the three elements (Pb, Sb, Sn) in oil painting and ceramic [20–22].

In samples g/32n and g33/n (Fig. 6), produced in the same ceramic laboratory (located at Santo Stefano di Camastra) around the year 2000, the selenium content, equal in the two tiles and slightly more

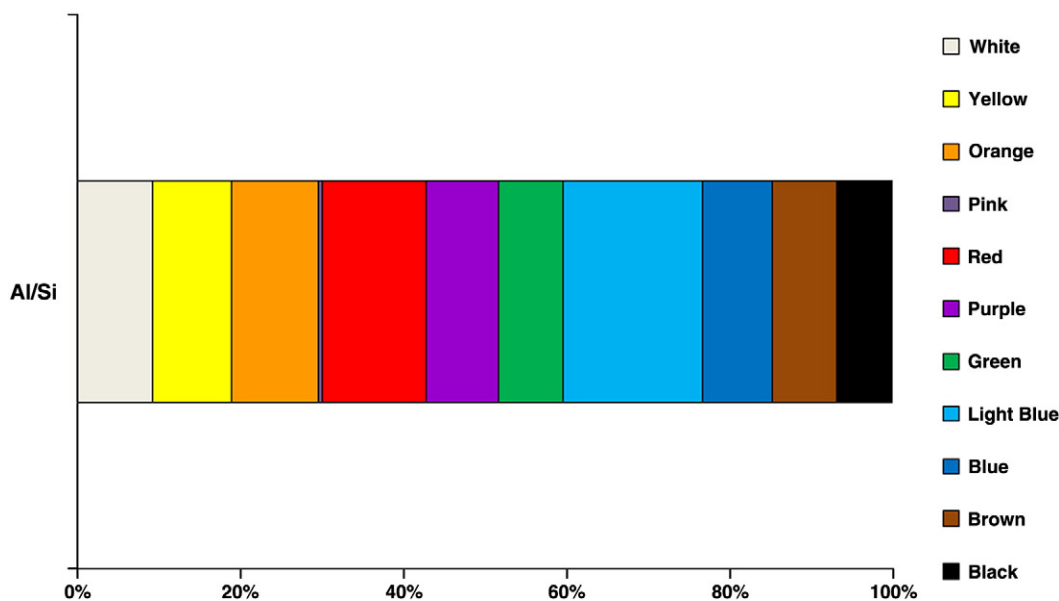


Fig. 3. Al/Si ratios in the different decorations.

abundant as compared to the other yellow samples, may be attributed to the use of a sulfo-selenide. This class of substances did not become commercially available as pigment until about the first quarter of the 20th century [23]. Traces of selenium present in all other samples can be attributed to impurities of the materials used in the preparation of pigments.

In samples g32/n and g33/n, the concentration of titanium (Ti/Si = 0.026 and 0.086), significantly higher as compared to all other samples, might be due to the use of TiO₂ to obtain the desired pastel shades. As in the case of blue samples (bl32/n and bl33/n), the compositions of the yellow decorations of the two tiles, produced in the same laboratory, are very similar.

In *light yellow decoration* gc/49a, where Fe is the principal element of coloring pigment, the concentration of Pb is much higher (Pb/Si = 0.24) than that in dark yellows (usually Pb/Si = 0.11). In this case the light

yellow color was obtained by adding white lead to an iron oxide (for example Yellow Mars). Considering the absence of antimony, we can exclude the use of Naples Yellow.

The *light blue tile decorations* contain opacifiers based on lead, aluminum and potassium whose amounts, normalized to silicon, respectively are 0.32, 0.16 and 0.093 and are characterized by presence of cobalt (Co/Si = 0.019) and very little Cu (Cu/Si = 0.0085) (Fig. 7). The pigment added in this case probably was *smalt*, a mixture containing cobalt oxide (*zaffre* or *zaffera*).

Although cobalt was isolated in the 18th century, its use (in the form of compounds or of ores) as pigment has been known for thousands of years because, even at low percentage, it produces a noticeable tint in an enamel [24]. Nearly all enamels develop a blue color with cobalt compounds, even in some conditions a pink one will develop as in sample p/57a in which the Co/Si ratio is much higher (0.15) compared

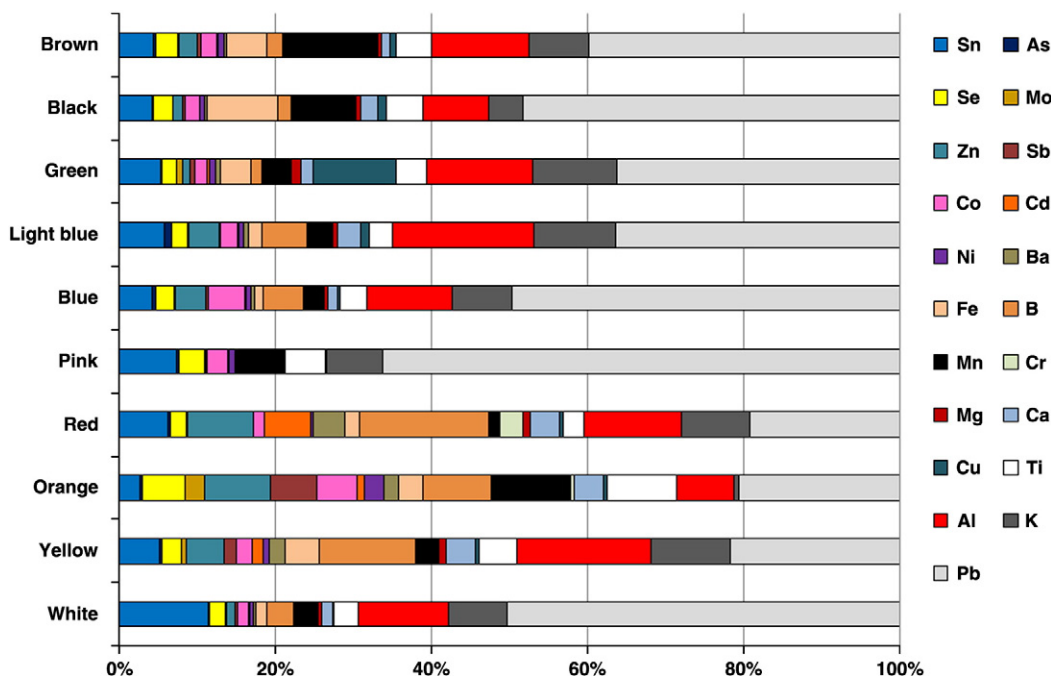


Fig. 4. Chemical composition of the colored decorations.

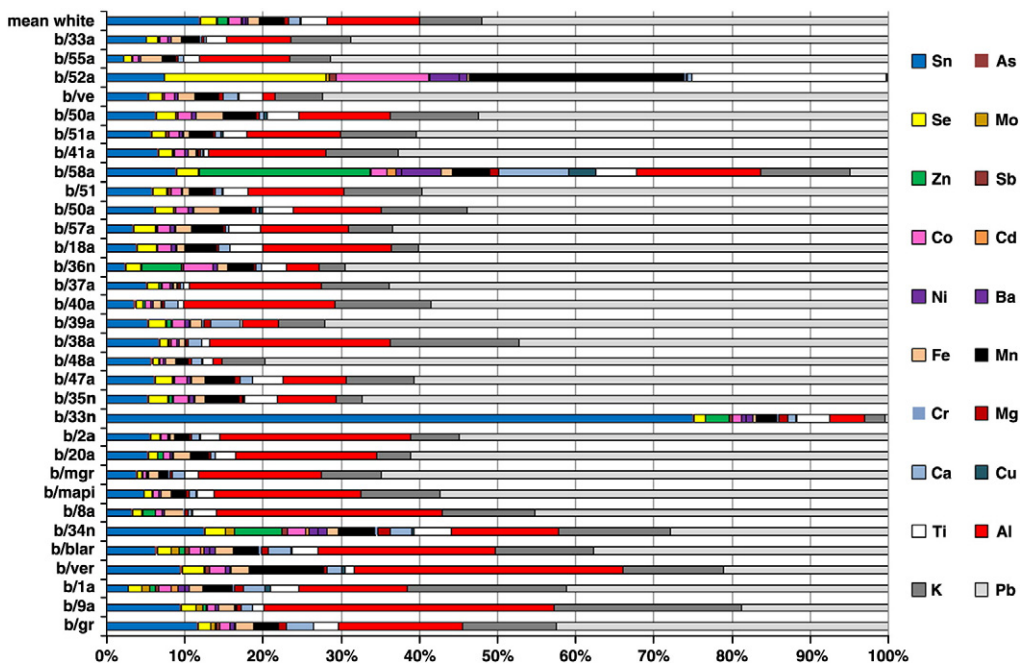


Fig. 5. Chemical composition of the white decorations.

to all the other samples with the exception of a single blue decoration (bl/41a). Several studies investigated the nature and origin of the cobalt minerals used to obtain deep blue pigments and are based on analysis of the elements associated with element [25,26].

Samples c58/a and c48/a differ from the other enamels because of their different composition. In sample c58/a, the concentration of copper, significantly higher ($Cu/Si=0.085$) as compared to all other samples, might be due to the use of pigments containing copper (CuO , $2CuCO_3 \cdot Cu(OH)_2$, chrysocolla, etc.) for its coloration, although the zinc ($Zn/Si=0.14$) and barium ($Ba/Si=0.029$) contents appear to be somewhat high. The last elements, as white zinc (ZnO) or

white fixed ($BaSO_4$), may have been used to obtain the desired hue. In sample c48/a, the concentrations of arsenic ($As/Si=0.078$), significantly higher as compared to all other samples (meanly $As/Si=0.0090$), might be due to the use of orpiment (As_2S_3) for its yellow coloration to obtain a greenish hue. The absence of copper excludes the use of green Scheele ($CuHAsO_3$). To our present knowledge, no data are published on the use of copper compounds in blue enamels.

The concomitant presence of Fe, Ni, Mn and As in our light blue samples is due to the fact that the pigments were most likely obtained by materials containing these elements. In particular, it is quite interesting to consider Co/As ratio values in order to better understand the

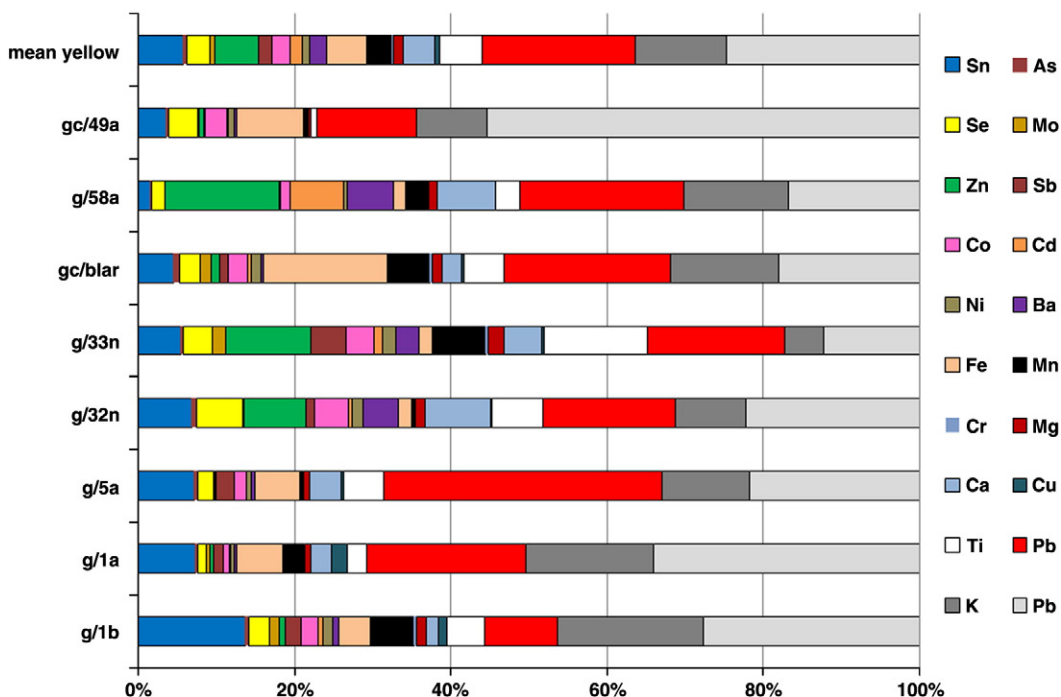


Fig. 6. Chemical composition of the yellow decorations.

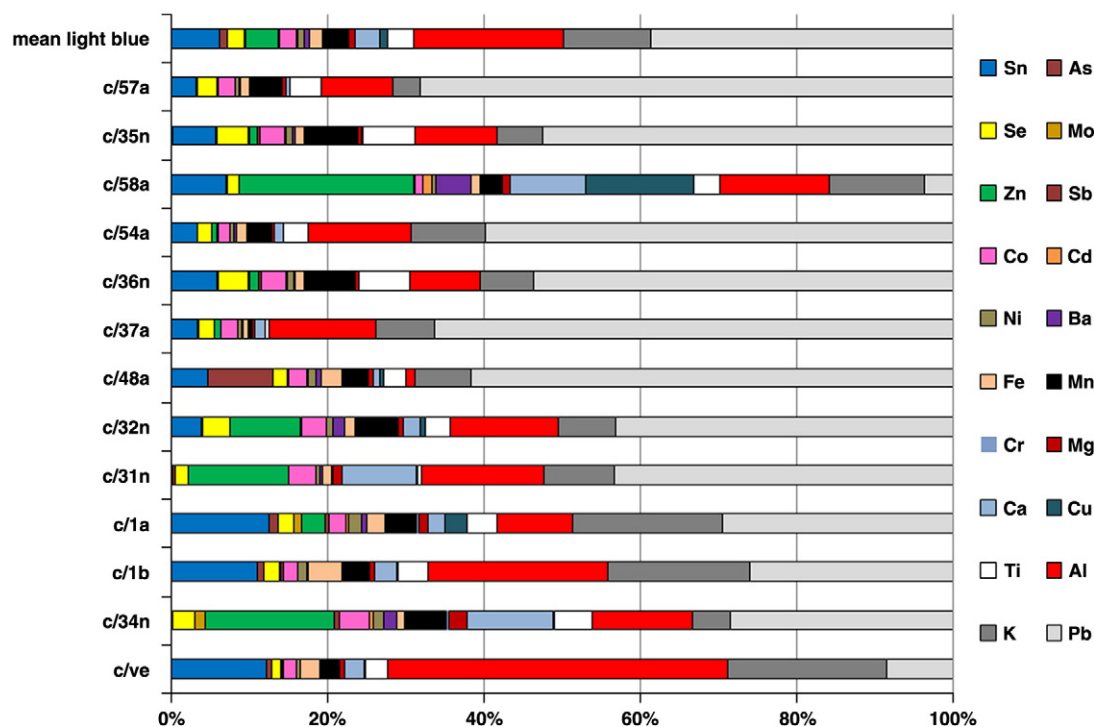


Fig. 7. Chemical composition of the light blue decorations.

technology used for the pigment preparation. Considering nine light blue samples, meanly, the high ratio ($Co/As = 13.6$) indicates that the firing conditions used during the production process were strong enough (oxidizing atmosphere and high temperature) to promote arsenic volatilization. In particular, we note that in very old samples (c/1a, c/1b e c/48a) ratios Co/As are very low (from 0.9 to 2.3). This confirms that the cobalt-containing pigments were not prepared or utilized in a sufficiently oxidizing environment to remove the arsenic.

Most of the blue decorations are characterized by relatively high cobalt ($Co/Si = 0.035$) and tin ($Sn/Si = 0.032$) contents. The blue

color of the decorations can be ascribed to the use of $CoO \cdot nSnO_2 + CoSn(OH)_6$ (Blue Cerulean) chromophore of high coloration power. These results are in good agreement with what several authors [27] refer for dark blue enamels, recommend saffre ($CoO +$ contaminant) or smalt ($SiO_2 - K_2O - CoO +$ contaminants) as coloring substance. From the 19th century, the authors prescribe pure industrial produced CoO [27]. Only Neri [27] suggested in some blue enamel the use of CuO .

The significant presence of molybdenum in only three blue samples (bl/34n, bl/33n and bl/32n) can be an indication that the pigment

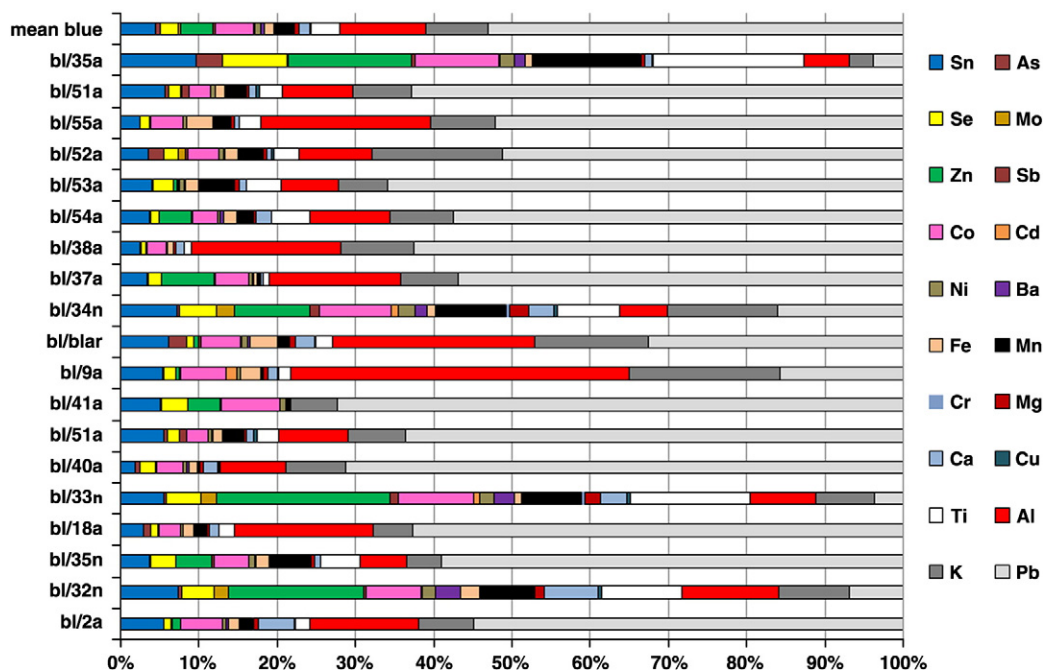


Fig. 8. Chemical composition of the blue decorations.

used in these areas was a compound termed *molybdenum blue* [28]. It's interesting to note that, for the same color of the decoration, tiles produced in the same geographic area (bl/34n, bl/33n and bl/32n) and in two different laboratories, have very similar composition (Fig. 8).

In the blue samples, cobalt appears linearly well correlated with nickel ($R^2=0.82$). It seems reasonable to associate these elements to impurities of cobalt pigments. This correlation is in good agreement to the fact that the traditional chromophore used for ceramic pigments with blue tint is the cobalt ion incorporated into different crystalline structures (silicate, alluminate, stannate, cromite, etc.) [29].

It is quite interesting to consider Co/As ratio values in order to better understand the technology used for the pigment preparation and to classify the tiles. For the blue decorations, the ratios ranged from 2.0 (sample bl/52a) to 46.1 (sample bl/55a). Low ratios indicate that the samples were not produced in recent years.

Green decorations, except for three samples (v/8a, v/blar, and vs/vec), contain considerable amounts of copper (Cu/Si = 0.055) (Fig. 9) suggesting the use of a large number of possible pigments. As one of the strongest coloring elements, Cu was one of the earliest colorants of enamels in early Egyptian ceramics. It produces a wide range of colors from greenish-blue to green and, in some cases, red depending upon composition and the firing atmosphere of the furnace. Probably green decorations have been obtained using copper oxide that may correspond to the pigment *ramina* utilized since the Middle Ages.

In all the samples, except in v/ve, only trace of antimony was detected, instead in the sample v/ve the presence of the element (Sb/Si = 0.0078) could indicate that lead antimonate was used.

Sample v/blar contains elevated quantities of Sn (Sn/Si = 0.27), Mn (Mn/Si = 0.025), Fe (Fe/Si = 0.022) and Co (Co/Si = 0.012) and very low copper amounts (Cu/Si = 0.0036). The green color could be thus a mixture of the yellow (Mars Yellow, Tin yellow, etc.) and blue pigments (Cerulean blue).

The dark green decoration of vs/vec sample contains low amounts of copper (Cu/Si = 0.020) and elevated amounts of lead (Pb/Si = 1.08), tin (Sn/Si = 0.066), manganese (Mn/Si = 0.040), arsenic (As/Si = 0.035) and cobalt (Co/Si = 0.030). Also in this case, to obtain the desired hue, the dark-green color could be produced with a

mixture of different pigments. In view of that, the intense green color of the later sample can be ascribed to the intentional addition of $\text{CoO} \cdot n\text{SnO}_2 + \text{CoSn}(\text{OH})_6$ (Blue Cerulean) in combination with As_2S_3 (Orpiment). In this case, considering that the antimony is present only in traces (Sb/Si = 0.0079), we can exclude the use of Naples Yellow [30,31].

The *light green decoration* vc/vec contains higher amounts of copper (Cu/Si = 0.049) and iron (Fe/Si = 0.062) than vs/vec (dark green). In this case, the light green color can be attributed to the addition of a pigment containing copper in combination with an iron base yellow compound. The absence of Cr in all the green enamels is an indication that no containing chrome pigments (Green of Guignet, green of Lamoriere, etc.) were used in the enamels of the investigated tiles. Also for green color, the relationship Co/As confirms the hypothesized dating by author for nine (v/ve, v/blar, v/1a, v/48a, v/52a, vc/vec, vs/vec, v/7a, v/50a) of the thirteen analyzed green decorations.

Only two *red decorations* (r/58a, r/15a) were analyzed. The red sample r/58a contained large amounts of Cd, (Cd/Si = 0.066) (Fig. 10) which suggests the use of the pigment CdS. Moreover, the presence of barium (Ba/Si = 0.043) and manganese (Mn/Si = 0.014) could suggest the use of low amounts of (psilomelane) $\text{Ba}(\text{Mn}^{2+})(\text{Mn}^{4+})_8\text{O}_{16}(\text{OH})_4$ or as $(\text{Ba},\text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$ to darken the red decoration (Fig. 1). Unusual is the composition of the red decoration r/15a, where chrome is present to a high level (Cr/Si = 0.032) which suggests the use of the red chrome pigment $(\text{Pb}_2(\text{OH})_2 \cdot \text{CrO}_4)$. Traces of cobalt were also found (Co/Si = 0.0090). An intentional addition of cobalt to obtain a darker hue of the red decoration seems likely.

The *pink decoration* of sample p57/a contained large amounts of Pb (Pb/Si = 3.7), Sn (Sn/Si = 0.41), Mn (Mn/Si = 0.33), Ti (Ti/Si = 0.29) and Se (Se/Si = 0.19) (Fig. 10). Moreover, the presence of manganese could suggest the contemporary use of low amounts of a brown pigment to darken the decoration.

From the decoration point of view, when a pastel color is required, as in the case of pink decoration, the ceramist adds an opacifier plus a pigment to the ceramic coating. For example, white lead could have been used in the sample p/57a. In this sample the ratio Pb/Si (Pb/Si = 3.7) is higher than that determined in the other colors (meanly Pb/Si = 1.03).

Observation of the data on *orange decoration* (Fig. 10) reveals a very similar composition to the yellow colored ones. Orange color

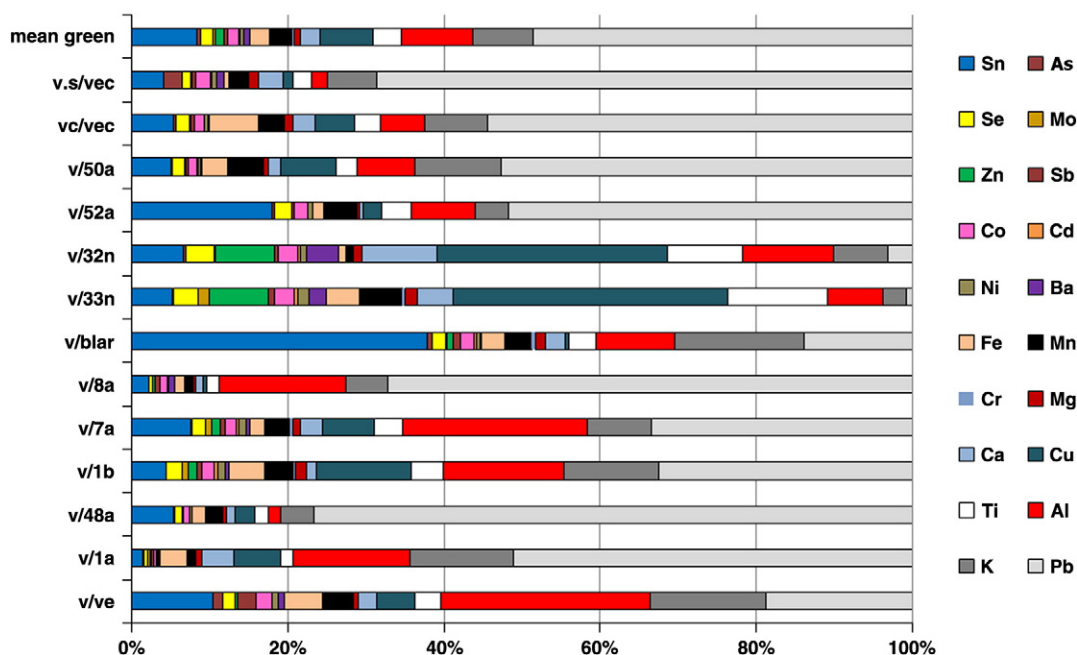


Fig. 9. Chemical composition of the green decorations.

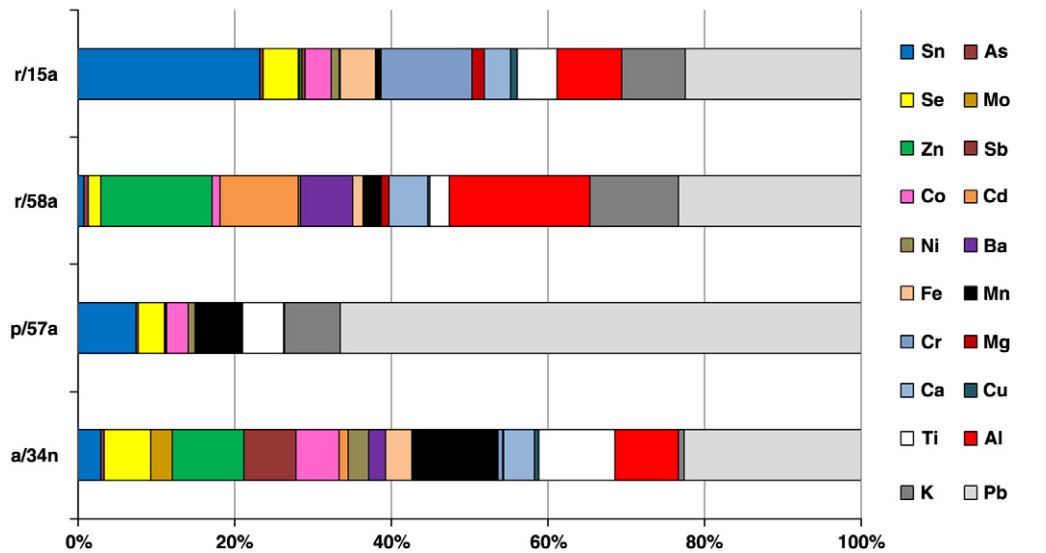


Fig. 10. Chemical composition of the orange ($\alpha/34n$), pink ($p/57\alpha$) and red ($r/58\alpha$, $r/15\alpha$) decorations.

present on sample $a/34n$, due to the high antimony concentration found ($Sb/Si = 0.082$), can be attributed to the use antimony orange ($Sb_2O_3 \cdot Sb_2S_3$), widely employed for ceramic decoration. As in the case of other pastel decorations, the ceramist added opacifiers to a pigment. For example, TiO_2 ($Ti/Si = 0.12$) could have been used in the sample $a/34n$. The presence of titanium confirms the hypothesized dating (21th century) for the sample 34n.

A set of tones between a dark brown and purple is found in the Sicilian tiles. Observation of the brown decorations reveals, except for a sample ($m/37a$) which has a color similar to purple to brown, a very similar chemical composition (Fig. 11) to the black-colored ones (Fig. 12).

Meanly, brown decorations contain considerable amounts of manganese ($Mn/Si = 0.076$) and iron ($Fe/Si = 0.032$) which suggests the

use of the pigments MnO_2 and Fe_2O_3 . Manganese exists in various oxidation numbers and imparts different derived colors. The tone of these colors in the decorations can be modified by furnace atmosphere. In an oxidant environment the color results pink, but, in a decoration, fired in a reducing atmosphere, deep greenish-brown colors predominate.

It's important to consider that three samples (having the same color) ($m/52$, $m/52a$, $ms/52$), taken from the same tile, show the same composition (Fig. 11). This demonstrates, once again, that the sampling method used by us in this research is reproducible.

Sample $m/37a$ differs from the other brown decorations because of its different tone and chemical composition. In this area, the amounts of zinc ($Zn/Si = 0.085$), cobalt ($Co/Si = 0.019$) and iron ($Fe/Si = 0.033$), significantly higher as compared to all other samples, may be due to

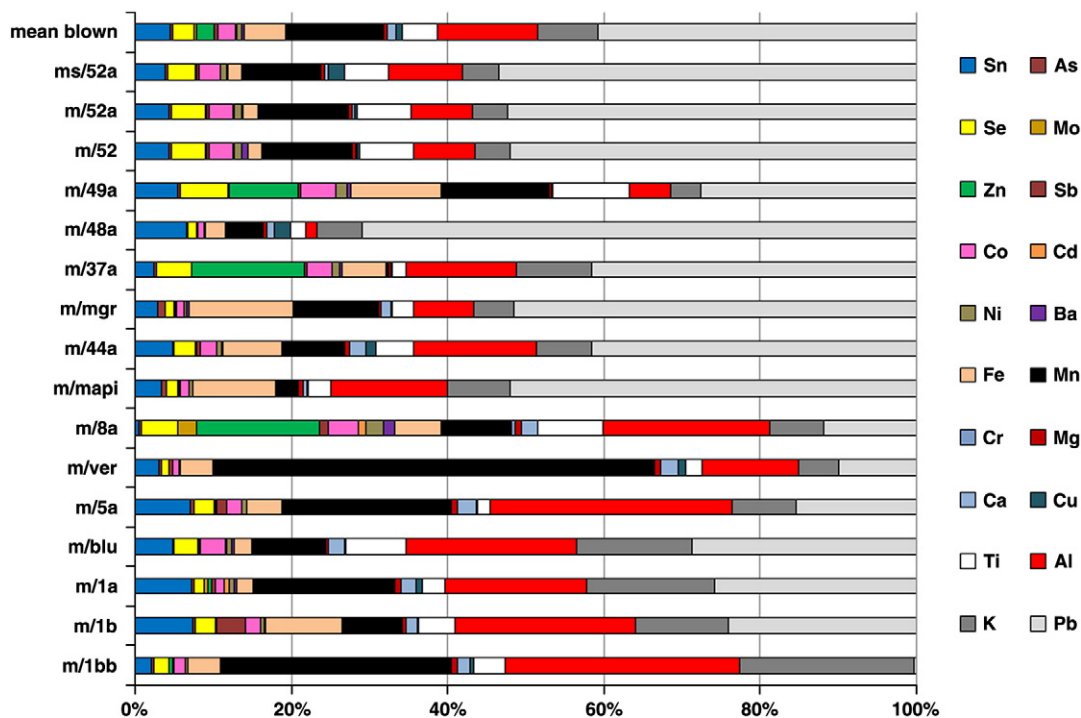


Fig. 11. Chemical composition of the brown decorations.

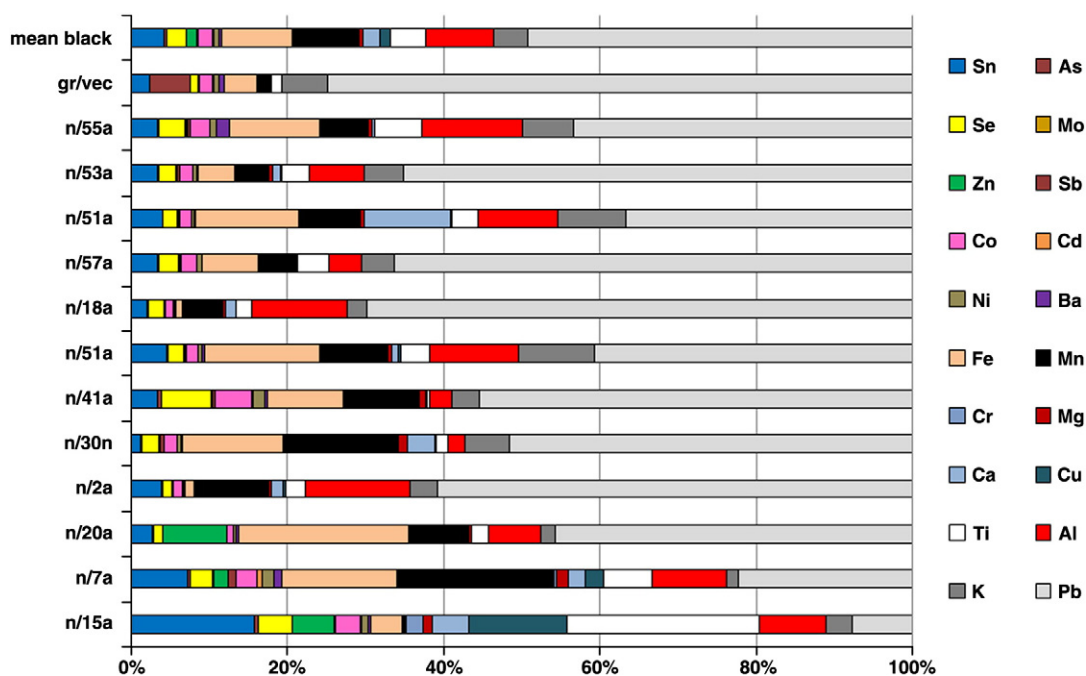


Fig. 12. Chemical composition of the black decorations.

the use of a natural ochre and then deliberately mixed by the ceramist with other pigments, for example zinc oxide and cobalt blue, in order to obtain the desired hues. Differently from all other brown enamels, the sample m/37a contains manganese only at trace levels ($Mn/Si = 0.002$).

The presence of barium ($Ba/Si = 0.008$) in sample m/8a could suggest the use of the mineral psilomelane as a source of manganese, and usually the absence of it implied the use of pyrolusite ($\beta\text{-MnO}_2$) [9].

Black decorations present in many of the analyzed tiles can be attributed to the use of an iron pigment such as Fe_2O_3 (Mars Black) deliberately mixed with MnO_2 (Manganese Black), widely employed as pigments for ceramic decoration, in fact the black enamels contain large amounts of iron ($Fe/Si = 0.068$) and manganese ($Mn/Si = 0.062$) (Fig. 11).

Gray decorations (gr/vec) contain considerable amounts of arsenic ($As/Si = 0.055$), iron ($Fe/Si = 0.047$), cobalt ($Co/Si = 0.020$) and manganese ($Mn/Si = 0.020$). Gray decoration is the most complex recipe, including, probably, four different pigments and several minor components in proportions to obtain the desired hue.

4. Conclusions

An analytical approach to the study of ancient tiles is relatively rare. In this study a total of 114 decorations of ceramic floor tiles, manufactured in Sicily in different times from the 16th to the 21st AD, were investigated. Only the ICP-OES technique was used in this study to investigate the elemental composition on the ceramic colored enamels. One of the advantages of the use of ICP-OES for this characterization is the better sensitivity attained, resulting in much improved limits of quantification, which can be particularly relevant for elements that are present at low levels in some of the samples, like chrome, arsenic, and molybdenum.

With the aim to gain some insight onto the practical aspects for sampling decorated tiles, experiments were conducted on different types of decorations (black, light blue and yellow). The micro sampling method, proposed by us, using a cotton swab soaked in hydrofluoric acid, includes advantages of high sensitivity, high selectivity, simplicity, speed, not expensive and can be considered non-destructive because

the point of sampling remains invisible to the human eye. The same procedures of sampling and analysis may be used to study enameled ceramics with different shapes and geographical origins (lustro, decorated ceramics from Central Italy, Portuguese Azulejos, Mexican ceramics, etc.).

Enameled decorations in Sicilian tiles were varied in tones and chromatic effects, obtained with a limited number compounds of cobalt, copper, iron, manganese, tin and in the artifacts following the year 1920, also titanium oxide.

An important remark is that some of the colors, such as black, orange, purple and brown were prepared using the same metals, while white, light blue, blue and green were obtained with different elements. Decorations were either composed of pure pigments or prepared as mixtures of pigments following several recipes, to obtain different hues and shades. The majority of the recipes are simple and involve one or two main pigments, sometimes with the addition of opacifiers and other minor components.

The adoption of different recipes for the same color suggests the presence of several laboratories of ceramists working in Sicily who had preferences for different methods for the production of their enameled artifacts.

The aluminum, in the form of oxide or hydroxide, was added to the pigments as a filler, or it is present together with Si, like in many other earth's samples analyzed by ICP-OES [7] as clay.

Concerning the opacifier, the high amounts of lead and antimony, in a case, indicate the use of lead antimonate ($Pb_2Sb_2O_7$).

Black decorations were present in several of the analyzed samples and in most of them were identified as being prepared with mixtures of black iron and manganese oxides. The green decorations appear to have been prepared with copper oxide; lighter hue samples contained additional amounts of zinc and/or barium compounds. Yellow decorations are present on many tiles. Considering all the samples, meanly, iron predominates in yellow decorations, only a sample contains large amounts of Cd, Zn and very little Sb, which suggests the use of the pigments ZnO (as white) and CdS as cadmium yellow. For all samples, except one, we can exclude the use of pigments containing chromium.

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