

# X-ray powder diffraction of mineral pigments and medicines from the 17<sup>th</sup> century pharmacy (*Spezieria*) *Santa Maria della Scala* in Rome, Italy

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The pharmacy (*spezieria*) *Santa Maria della Scala* was founded in Rome by the Discalced Carmelites Order in the 17<sup>th</sup> century, and during the 18<sup>th</sup> and 19<sup>th</sup> centuries it became the official supplier of medicines for Vatican Popes. The laboratory and the cases of this *spezieria* still preserve glass jars with organic and inorganic materials, which were presumably used for medicine and artistic material preparation, whose composition is unknown to date. A research project was initiated with the aim to study the stored materials and the role that the pharmacy played in regional, national and international contexts. In this manuscript, the compounds were analysed through X-ray powder diffraction with the scope to derive the quantitative mineralogical composition of the inorganic fraction, their possible use in pharmacopoeias and as mineral pigments. Most of the analysed samples are salts (sulphates, chlorides, carbonates, phosphates, borates, sulphides), sulphates being the predominant class; oxides were also detected. © 2018 International Centre for Diffraction Data.

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## I. INTRODUCTION

Convent pharmacies played a pivotal role in Renaissance Italy by producing and marketing medicines to public (Strocchia, 2011). In the late 17<sup>th</sup> century, there were 45 convent pharmacies in Rome. Roman people preferred these establishments to the secular pharmacies that proliferated since the beginning of the 15<sup>th</sup> century because they sold their medicines more cheaply and sometimes for free. This was possible because convent pharmacies were exempted in paying taxes. On the contrary, secular establishments had to pay taxes and this fact explains why their owners complained to the *Collegio degli Speziali Romano*, arguing that convent pharmacies or *spezierie* had to be closed. According to their arguments, convent pharmacies did not respect both the *Antidotarium romanum* (the fixed price for each medicine) and the *rerum petendarum*, being able to sell substances that could represent a health hazard (Colapinto, 2007). Since 1722–1735, several decrees prohibited convent pharmacies to selling all types of medicine except apoplastic balsam and the well-known antidote *Theriaca* (Colapinto, 2007). Certain religious establishments, however, were unaffected by these decrees thanks to the importance they had acquired in 18<sup>th</sup> century Rome. Among these establishments, two convent pharmacies were founded by the Discalced Carmelites. An authorization granted by Pope Alexander VI (1492–1503) enabled this religious order of Spanish origin to find, some

years later, a pharmacy in the convent *Santa Maria della Vittoria* and another in the convent *Santa Maria della Scala* (Pedrazzini, 1934). Undoubtedly, the latter became very famous in Rome during the 18<sup>th</sup> and 19<sup>th</sup> centuries, when it was frequented not only by the humble classes but also by the nobility and church dignitaries. Indeed, in 1829, Pope Pius VIII awarded the pharmacy *Santa Maria della Scala* the privilege to becoming the Roman supplier of medicines for the Pontiff, the Pontiff's family, and the Swiss Guard (Spotti, 2007). For this reason, the pharmacy continued the activity throughout the 19<sup>th</sup> century and until the middle of the 20<sup>th</sup> century.

The research project entitled *Antichi Minerali nell'arte degli Speziali di "De Medicamentaria Officina" di Santa Maria della Scala: indagini Chimico-Fisiche e studio Storico-Culturale* (Ancient minerals in the "pharmaceutical laboratory" of *Santa Maria della Scala*: physical–chemical analysis and historical–cultural research) was designed for the following scopes:

- To perform physical–chemical identification of 231 medicines preserved in their jars in this ancient Roman pharmacy (Figure 1) for understanding their composition and the chemical formulation;
- To identify the range of medical knowledge gathered at this Roman convent pharmacy from the ancient Mediterranean area (especially Greece), the ancient Middle East and Egypt, a wealth of which trickled through to the Modern Era via the Islamic tradition as, in the 17<sup>th</sup> and 18<sup>th</sup> centuries, the Order of the Discalced Carmelites controlled the trading

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Figure 1. Pharmacy (*spezieria*) Santa Maria della Scala, Rome (Italy). Interior of the main hall.

routes towards the Far East and the New World (Zupanov and Barreto, 2014).

- To understand the use of the stored compounds as medicines and artistic materials (it is not surprising that, from the Middle Ages to the Renaissance, painters and pharmacists were members of the same guild as in the 15<sup>th</sup> century Florence, for instance).

The specific focus of this research paper is the Quantitative Phase Analysis (QPA) of the inorganic fraction of about 100 compounds in order to know the amount of each mineral in the polycrystalline mixtures. In addition, the following issues have been tackled: the relationship between the label reported on the glass jar and the mineralogical composition, the amount of specific mineralogical groups, their use as mineral medicines, and/or mineral pigments.

## II. MATERIALS AND METHODS

The analysed samples are listed in Table I including the label reported on the glass container, the full name found in treatises (Paláu y Verdéra, 1784; Hernández de Gregorio, 1803; Carbonell, 1805; Gray, 1821), and the mineralogical composition. The samples discussed here represent about 70% of the (primarily) inorganic materials available at the pharmacy; the remaining 30% samples will be the object of further in-depth studies, also using complementary analytical techniques.

X-ray powder diffraction (XRPD) was carried out on randomly oriented samples after grinding the powder samples in an agate mortar. A Bruker D8 Advance system, operating in  $\theta$ :  $\theta$  mode was used; generator setting 40 kV, 40 mA, Cu anode ( $\text{CuK}\alpha = 1.5418 \text{ \AA}$ ), Ni filter,  $2\theta$  range 5–80°, step size 0.01°, scan speed 0.5° min<sup>-1</sup>. Qualitative phase determination was carried out using the software QualX2.0 (Altomare *et al.*, 2015) and the correlated COD database (Gražulis *et al.*, 2009). QPA was carried out using the software Quanto (Altomare *et al.*, 2001).

## III. RESULTS

Mineral phase identification and QPA of polycrystalline mixtures are listed in Table I.

Results of the mineral phases will be presented according to their chemical group.

*Sulphates.* Most of the mineralogical species belonging to sulphates and reported with different identification names in Table I is composed of arcanite ( $\text{K}_2\text{SO}_4$ ). In 71 samples, arcanite is an individual phase with very sharp reflections indicating a well-crystallized material [Figure 2(a)]. In three samples (samples 15, 110, and 214), arcanite is associated with sylvite (KCl) and apthitalite [ $\text{NaK}_3(\text{SO}_4)_2$ ]. In particular, in the sample 110, arcanite is the principal component (87%), whilst in the samples 214 and 15, it is an accessory mineral (6 and 7%, respectively).

Alum-K, a hydrated (KAl)-sulphate with chemical formula  $\text{KAl}(\text{SO}_4)_2 \cdot 12(\text{H}_2\text{O})$  is the individual mineralogical phase detected in the sample 94. It was also detected in *Pietra divina* [sample 98; Figure 2(b)] where it is associated with kaliochalcite  $\text{KCu}_2(\text{SO}_4)\text{OH}$  and nitre  $\text{KNO}_3$  (Table I), with the following proportions: alum-K = 35%; kaliochalcite = 35%; nitre = 30%.

*Chlorides.* Halite (NaCl) is the individual constituent of sample 62 and it is associated with sylvite (KCl) in the sample 71 (halite = 97%; sylvite = 3%). Calomel ( $\text{Hg}_2\text{Cl}_2$ ) is the individual constituent of the sample 35, whilst in the sample 122, it is associated with an Hg-oxychloride, eglestonite, with formula  $[\text{Hg}_2]_3\text{Cl}_3\text{O}_2\text{H}$  (Mereiter *et al.*, 1992), with the following proportion: eglestonite = 85%; calomel = 15%. Finally, the ammonium chloride salt ( $\text{NH}_4\text{Cl}$ ) was identified as the individual component of the sample 205.

*Carbonates.* Ca-carbonates occur in the samples 70 and 116 where the two polymorphs (rhombohedral) calcite and (orthorhombic) aragonite with chemical formula  $\text{CaCO}_3$  are simultaneously present. In these samples, aragonite is the primary mineralogical phase (Table I). Hydrated Pb-carbonate hydrocerussite [ $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ] was detected in the sample 73 (80%) associated with 20% of the anhydrous equivalent ( $\text{PbCO}_3$ ).

TABLE I. Quantitative Phase Analysis (QPA) of the analysed samples.

ID	Label on the container	Full transcription of the label	Minerals (QPA)
1	Sal. Vener	<i>Sal Veneris</i>	Arcanite
2	Sal Pimpinell	<i>Sal Pimpinellae</i>	Arcanite
4	Sal Guajac	<i>Sal Guajaci</i>	Arcanite
9	Sal Escorz Ner	<i>Sal Scorzonerae Nera</i>	Arcanite
10	Sal Beccabung	<i>Sal Beccabungae</i>	Arcanite
11	Sal Hyosciam	<i>Sal Hyosciamus</i>	Arcanite
12	Sal Ormin	<i>Sal Hominun</i>	Arcanite
13	Sal Peon	<i>Sal Peoniae</i>	Arcanite
15	Sal Juvartel	<i>Sal Juvartel</i>	Sylvite (48%), apthitalite (45%), arcanite (7%)
16	Sal Eliotrop	<i>Sal Heliotropium</i>	Arcanite
17	Sal Asparag	<i>Sal Asparagus</i>	Arcanite
21	Sal Caryoph	<i>Sal Caryophyllorum</i>	Arcanite
22	Sal Dictam Cret.	<i>Sal Dictamnus Creticus</i>	Arcanite
24	Sal Polychr	<i>Sal Polychrestus (Glaseri)</i>	Arcanite
29	Sal Absynt	<i>Sal Absinthii</i>	Arcanite
31	Pulv. Cahet. Arnol	<i>Pulvis (?)</i>	Hematite
33	Sal Centaur	<i>Sal Centauri Minoris</i>	Arcanite
35	Princip. Alb.	<i>Praecipitato Albae</i>	Calomel
45	Sal Tanasell	<i>Sal Tanacetum</i>	Arcanite
46	Sardon	Sardon	Quartz
52	Sal Tartar Solub.	<i>Sal Tartari Solubile</i>	Arcanite
53	Sal Anonid	<i>Sal (?)</i>	Arcanite
54	Sal Capill Vener	<i>Sal Capillus Veneris</i>	Arcanite
58	Sal Agrimon	<i>Sal Agrimoniae</i>	Arcanite
60	Sal Rest. Capr.	<i>Sal Restictivus Caprifolium</i>	Arcanite
61	Sal Scabios	<i>Sal Scabiosae</i>	Arcanite
62	Sal Apet	<i>Sal (?)</i>	Halite
65	Sal Alchimill	<i>Sal Alchemilla</i>	Arcanite
68	Sal Goniz	<i>Sal (?)</i>	Arcanite
70	Margarit	<i>Margaritaria Nobilis</i>	Aragonite (95%), calcite (5%)
71	Sal Fenaot	<i>Sal (?)</i>	Halite (97%), sylvite (3%)
72	Sal Junyp	<i>Sal Juniper</i>	Arcanite
73	Trocisc. Alb. Rax.	<i>Trochisci Albayalde (?)</i>	Hydrocerrusite (80%), cerussite(20%)
76	Anacard	<i>Anacardium</i>	Arcanite
78	Sal Carlin	<i>Sal Carlina</i>	Arcanite
79	Sal Androsdem	<i>Sal (?)</i>	Arcanite
84	Sal Tartar F.	<i>Sal Tartari Factitius</i>	Arcanite
91	Sal Chichor	<i>Sal Chicheros</i>	Arcanite
94	Especific. Elvet.	<i>Especific (?) Helvetii</i>	Alum
96	Sal Balsamin	<i>Sal Balsamina</i>	Arcanite
97	Sal Achant	<i>Sal Acanthium</i>	Arcanite
98	Pietra divina	<i>Pietra divina</i>	Alum (35%), nitre (30%), kaliocalcite (35%)
102	Sal. Digest. Sylv.	<i>Sal Digestivus Sylvestrium</i>	Arcanite
109	Cinbr. Antymon.	<i>Cinnabaris antimonii</i>	Cinnabar
110	Sal. Anet	<i>Sal Anethum</i>	Arcanite (87%), apthitalite (13%)
113	Corn. Cerv. PR.	<i>Cornu Cervi Praeparatus</i>	Hydroxylapatite
116	Mutriforte Palay?	<i>(?)</i>	Aragonite (86%), calcite (14%)
122	Mercurio Solub. del Mosc	<i>Mercurio Solubile Moschus</i>	Eglestonite (85%), calomel (15%)
124	Sal Mirabit.	<i>Sal Mirabilis Glauberi</i>	Arcanite
125	Sal Aquileg	<i>Sal Aquilegia</i>	Arcanite
127	Ossido di Megane	<i>(?)</i>	Quartz, bixbyte and?
131	Sal Mynsich	<i>Sal Mynsichti</i>	Arcanite
133	Sal Cyan	<i>Sal Cyanus</i>	Arcanite
134	Sal Barden	<i>Sal Bardana</i>	Arcanite
136	Sal. Corocop	<i>Sal (?)</i>	Arcanite
137	Anthiomet. P.P.	<i>(?)</i>	Cassiterite and?
138	Calomel Turc.?	<i>Calomel Turc.(?)</i>	Hydroxylapatite
140	Protossido di Piombo	<i>Protossido di Piombo</i>	Litharge and?
144	Sal Hyperic	<i>Sal Hypericum</i>	Arcanite
146	Sal. Card. Benect.	<i>Sal Cardui Benedicti</i>	Arcanite
147	Sal Eder. Terr	<i>Sal Hedera Terrestris</i>	Arcanite
148	Cinabr. Nativ.	<i>Cinnabaris Native</i>	Cinnabar
151	Sal Herniar	<i>Sal Herniaria</i>	Arcanite
152	Cinabr. Fact.	<i>Cinnabaris factitia</i>	Cinnabar
154	Sal Betton	<i>Sal Betonica</i>	Arcanite
155	Sal Chin.	<i>Sal China</i>	Arcanite

Continued

TABLE I. Continued

ID	Label on the container	Full transcription of the label	Minerals (QPA)
156	Sal Tanacet	<i>Sal Tanacetum</i>	Arcanite
157	Sal Lentise	<i>Sal Lentiscus</i>	Arcanite
158	Sal Taraxac	<i>Sal Taraxacum</i>	Arcanite
159	Sal Soldanell	<i>Sal Soldanella</i>	Arcanite
161	Sal Parietar	<i>Sal Parietariae</i>	Arcanite
163	No label	<i>No label</i>	Monetite
168	Sal Mart	<i>Sal Martis</i>	Arcanite
169	Sal Alliar	<i>Sal Alliariae</i>	Arcanite
172	Sal Feber	<i>Sal (?)</i>	Arcanite
175	Semi di Felandro Aquatico	<i>Semina di Feladrio Aquatico</i>	Arcanite
179	Sal. Acler. Terr	<i>Sal (?)</i>	Arcanite
180	Sal Genist	<i>Sal Genistae</i>	Arcanite
183	Sal Polii Mont.	<i>Sal (?)</i>	Arcanite
184	Sal Bistort	<i>Sal Bistortae</i>	Arcanite
187	Borat Sod.	<i>Borax Sodae</i>	Tintalconite
194	Sal Absynt	<i>Sal Absinthii</i>	Arcanite
196	Sal Abrotan	<i>Sal Abrotanum</i>	Arcanite
203	Pulv. Astringent	<i>Pulvis Astringent</i>	Jarosite (66%), goethite (34%)
204	Sal [. . .]	<i>Sal [. . .]</i>	Arcanite
205	F. Hydroc. Amm.	<i>Ferrum Hydrocharis Ammoniacale</i>	Sal Ammoniac
206	Sal Agrimon	<i>Sal Agrimoniae</i>	Arcanite
207	Sale di Card. Benect	<i>Sal Cardui Benedicti</i>	Arcanite
208	Sal Alchecheg	<i>Sal (?)</i>	Arcanite
209	Sal Acanth	<i>Sal Acanthium</i>	Arcanite
210	Sal Tanacet	<i>Sal Tanacetum</i>	Arcanite
212	Sal Nasturt Aq.	<i>Sal Nasturtium aquaticum</i>	Arcanite
214	Sal Theriacal	<i>Sal Theriacalis</i>	Sylvite (48%), apthitalite (46%), arcanite (6%)
215	Sal Fragor	<i>Sal Fragorum</i>	Arcanite
217	Sal Fabar	<i>Sal Fabarum</i>	Arcanite
218	Magist. Mart. Ap.	<i>Magisterium Martis</i>	Maghemite?, magnetite?
220	Arcanum [. . .]	<i>Arcanum [. . .]</i>	Arcanite
221	Sal Pimpinell	<i>Sal Pimpinella</i>	Arcanite
222	Lap. Hematit. PP.	<i>Lapis Ematite</i>	Hematite

(?) = full transcription is not known.

**Phosphates.** Ca-phosphate was detected in the samples 113 and 138 as hydroxylapatite, the latter displaying very low crystallinity. The sample 163 is composed of monetite with chemical formula  $\text{CaHPO}_4$ .

**Borates.** One sample (187) is composed of tintalconite [Figure 2(c)], a hydrated Na-(tetra)borate with chemical formula  $\text{Na}_2(\text{B}_4\text{O}_7) \cdot 5\text{H}_2\text{O}$ .

**Oxides.** Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) is the individual constituent of the samples 31 and 222. The low crystallinity of the sample 218 does not allow for a clear distinction between maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ), though it is possible they are co-present as a result of aerial oxidation (Frison *et al.*, 2013).

Quartz ( $\text{SiO}_2$ ) is the mineral detected in the sample 46. It is associated with bixbyite ( $\text{FeMnO}_3$ ) in the sample 127. Mineral cassiterite with chemical formula  $\text{SnO}_2$  is the constituent of the sample 137. For the samples 127 and 137, QPA was not possible because there are other minerals whose identification is not clear.

**Sulphides.** The mineral cinnabar ( $\text{HgS}$ ) was identified in the samples 109, 148, and 152 as individual mineral.

**Mixtures.** Mixtures of salts have been discussed earlier in the sulphate group. The remaining samples 140 and 203 [Figure 2(d)] are, respectively, composed of litharge ( $\text{PbO}$ ) associated with undetected minerals, and jarosite in combination with goethite ( $\alpha\text{-FeOOH}$ ), with the following proportion: jarosite = 66%; goethite = 34%.

## IV. DISCUSSION

The mineralogical analysis carried out on 99 inorganic samples collected from the glass containers stored in the laboratory of the pharmacy *Santa Maria della Scala* in Rome allowed for a clear definition of the mineralogical nature of the studied materials.

The most immediate evidence emerged after the interpretation of the XRPD profiles is that the inorganic fractions of almost all the analyzed samples are primarily in the form of salts (92% of the total analyzed in the present study) and the remaining are oxides and mixtures of different chemical compounds [Figure 3(a)].

Most of the analyzed salts are sulphates [81%; Figure 3(b)] and almost all are in the form of arcanite ( $\text{K}_2\text{SO}_4$ ), generally detected as individual mineral. The name of this salt derives from the Latin *Arcanum duplicatum* (double secret), a Medieval alchemical name, and was given for the first time by the mineralogist W. K. von Haidinger in 1845 (Frondele, 1950).

In nature, this mineral is associated with deposits from fumaroles and hot springs. High contents of arcanite were found in exhalations of the Arsenatnaya fumarole, Tolbachik Volcano in Russia associated with langbeinite, apthitalite, hematite, tenorite, and others (Zubkova *et al.*, 2018). Arcanite can be manufactured from sylvite and a sulphate component in a single or multistage process,



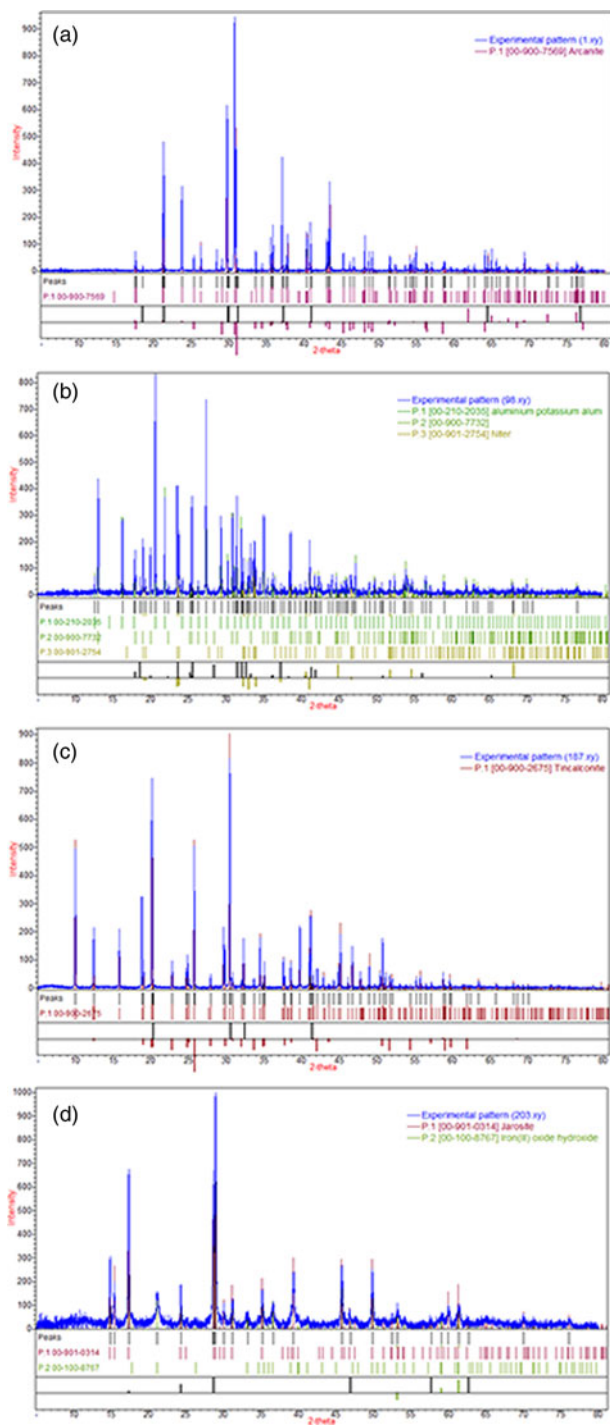


Figure 2. XRPD profiles of selected samples. (a) Arcanite (sample 1); (b) *Pietra divina* composed of alum-K, nitre, and kaliochalcite (sample 98); (c) tinalconite (sample 187); (d) jarosite and goethite (sample 203).

according to the following reaction (Fezei *et al.*, 2008a, 2008b)



As reported in Goncharik *et al.* (2014), the process was developed by Kurnakova and Luk'yanova and first published in 1949.

The production of salts by plants as reported in Junius (1986) requires further in-depth studies.

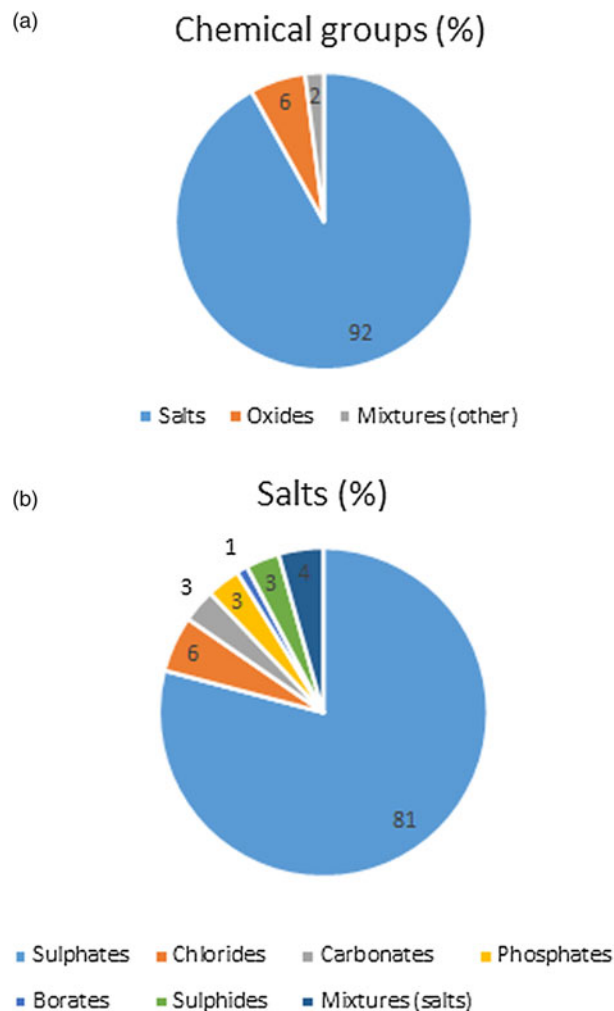


Figure 3. Grouping of the analysed samples. (a) Chemical groups identified after XRPD; (b) chemical composition of the diverse detected salts.

The intriguing question is to understand the reason why the same mineral arcanite is listed with different names as in Table I. The most plausible reason is that the same salt was used as a vehicle for organic compounds thus explaining the various colours of the same and nominally white chemical compound. In fact, the various names (of arcanite) are tied to those of plants and flowers (Paláu y Verdéra, 1784) as reported, for most of them, in Table II. Some of these label inscriptions suggest that ancient deities, planets, or luminaries were indeed incidental in the name given to the drug and probably inspired its alleged therapeutic properties. Inscriptions such as the abbreviation “Mart” (i.e. sample 218), “Ven(er)” (i.e. sample 1), “Juvartel” are a clear reference to the deity and planets Mars, Venus, and Jupiter. The name of these salts recall mythological Greco-Roman beliefs, as also occurs with the rest of the drugs conserved (Vázquez de Ágredos Pascual *et al.*, 2017, 2018).

The hydrated sulphates are in the form of alum-K (Al, K-sulphate) and jarosite (K,Fe-sulphate). Potash alum has been used as an ingredient (reagent to form the substrate for dyestuff) in recipes for the production of red lake pigments in Western Europe easel painting since the 12<sup>th</sup> century (Kirby *et al.*, 2005). In addition, K-alum is an extremely astringent compound. Ancient medical and health care professionals often used it to treat injuries and illness as it is

TABLE II. Full transcription of the (medicinal) salts and correlation with flowers and plants.

ID	Full transcription of the label	Aromatic compounds of the salts (according to their name)
1	<i>Sal Veneris</i>	<i>Adiantum capillus-veneris</i> L. <i>Scandix pecten veneris</i> L. <i>Umbelicus rupestris</i>
2	<i>Sal Pimpinellae</i>	<i>Pimpinella anisum</i> L. <i>Pimpinella lutea</i> L. <i>Pimpinella saxifraga</i> L. <i>Sanguisorba minor</i> Scop.
4	<i>Sal Guajaci</i>	<i>Couroupita guianensis</i> Aubl. <i>Guajacum officinale</i> L.
9	<i>Sal Scorzonerae Nera</i>	<i>Scorzonera hispanica</i> L.
10	<i>Sal Beccabungae</i>	<i>Veronica becabunga</i> L. <i>Veronica anagallis aquatica</i> L.
11	<i>Sal Hyoscyamus</i>	<i>Hyoscyamus niger</i> L. <i>Hyoscyamus albus</i> L.
12	<i>Sal Horminum</i>	<i>Salvia verbenaca</i> L. <i>Salvia viridis</i> L.
13	<i>Sal Peoniae</i>	<i>Paeonia</i> L.
16	<i>Sal Heliotropium</i>	<i>Heliotropium indicum</i> L. <i>Heliotropium supinum</i> L. <i>Heliotropium europaeum</i> L.
17	<i>Sal Asparagus</i>	<i>Asparagus officinalis</i> L. <i>Asparagus acutifolius</i> L. <i>Syzygium aromaticum</i> L.
21	<i>Sal Caryophyllorum</i>	<i>Dictamnus albus</i> L.
22	<i>Sal Dictamnus Creticus</i>	<i>Potassae polychrestus</i> (Glaseri)
24	<i>Sal Polychrestus (Glaseri)</i>	<i>Artemisia absinthium</i> L.
29	<i>Sal Absinthii</i>	<i>Potassae centaury minoris</i>
33	<i>Sal Centauri Minoris</i>	<i>Tanacetum balsamita</i> L. <i>Tanacetum vulgare</i> L. <i>Tanacetum annuum</i> L.
45	<i>Sal Tanacetum</i>	<i>Morus alba</i> L.
52	<i>Sal Tartari Solubile</i>	<i>Adiantum capillus-veneris</i> L.
54	<i>Sal Capillus Veneris</i>	<i>Agrimonia eupatoria</i> L.
58	<i>Sal Agrimoniae</i>	<i>Lonicera periclymenum</i> L.
60	<i>Sal Restictivus Caprifolium</i>	<i>Knautia arvensis</i> (L.) Coult. <i>Succisa pratensis</i> Moench. <i>Scabiosa atropurpurea</i> L.
61	<i>Sal Scabiosae</i>	<i>Alchemilla vulgaris</i> L. <i>Alchemilla alpina</i> L.
65	<i>Sal Alchemilla</i>	<i>Juniperus communis</i> L. <i>Juniperus oxycedrus</i> L. <i>Juniperus thurifera</i> L. <i>Juniperus phoenicea</i> L. <i>Juniperus sabina</i> L.
72	<i>Sal Juniper</i>	<i>Carlina vulgaris</i> L. <i>Carlina acaulis</i> L. <i>Carlina acanthifolia</i> All. <i>Morus alba</i> L.
78	<i>Sal Carlina</i>	<i>Cicer arietinum</i> L.
84	<i>Sal Tartari Factitius</i>	<i>Momordica balsamina</i> L.
91	<i>Sal Chicheros</i>	<i>Onopordum acanthium</i> L.
96	<i>Sal Balsamina</i>	<i>Foeniculum vulgare</i> Mill. <i>Anethum graveolens</i> L.
97	<i>Sal Acanthium</i>	<i>Mirabilis jalapa</i> L. <i>Mirabilis longiflora</i> L. <i>Mirabilis dichotoma</i> L.
110	<i>Sal Anethum</i>	<i>Ligusticum aquilegifolium</i> (All.) Willd. <i>Aquilegia vulgaris</i> L.
124	<i>Sal Mirabilis Glauberi</i>	<i>Potassae Mynsichti</i> <i>Centaurea cyanus</i> L. <i>Bardana minor</i> Hill.
125	<i>Sal Aquilegia</i>	<i>Hypericum androsaemum</i> L. <i>Hypericum perforatum</i> L.
131	<i>Sal Mynsichti</i>	<i>Potassae Cardui Benedicti</i>
133	<i>Sal Cyanus</i>	<i>Hedera helix</i> L.
134	<i>Sal Bardana</i>	<i>Glechoma hederacea</i> L.
144	<i>Sal Hypericum</i>	
146	<i>Sal Cardui Benedicti</i>	
147	<i>Sal Hedera Terrestris</i>	

Continued

TABLE II. Continued

ID	Full transcription of the label	Aromatic compounds of the salts (according to their name)
151	<i>Sal Herniaria</i>	<i>Herniaria glabra</i> L. <i>Herniaria hirsuta</i> L.
154	<i>Sal Betonica</i>	<i>Stachys officinalis</i> (L.) Trevis. <i>Betonica aquatica</i> (Beto.)
155	<i>Sal China</i>	<i>Terminalia Vernix</i>
156	<i>Sal Tanacetum</i>	<i>Tanacetum balsamita</i> L.
157	<i>Sal Lentiscus</i>	<i>Pistacia lentiscus</i> L.
158	<i>Sal Taraxacum</i>	<i>Leontodon taraxacum</i> L.
159	<i>Sal Soldanella</i>	<i>Soldanella alpina</i> L. <i>Convolvulus soldanella</i> L.
161	<i>Sal Parietariae</i>	<i>Parietaria officinalis</i> L.
168	<i>Sal Martis</i>	From iron
169	<i>Sal Alliariae</i>	<i>Adenostyles alliariae</i>
175	<i>Semina di Feladrio Aquatico</i>	<i>Oenanthe aquatica</i> (L.) Poir
180	Sal Genistae	<i>Genista germanica</i> L. <i>Genista Canariensis</i> L. <i>Genista tinctoria</i> L.
184	<i>Sal Bistortae</i>	<i>Polygonum Bistorta</i> L.
194	<i>Sal Absinthii</i>	<i>Artemisia Absinthium</i> L.
196	<i>Sal Abrotanum</i>	<i>Artemisia Abrotanum</i> L.
206	<i>Sal Agrimoniae</i>	<i>Agrimonia Eupatoria</i> L.
207	<i>Sal Cardui Benedicti</i>	<i>Potassae Cardui Benedicti</i>
209	<i>Sal Acanthium</i>	<i>Onopordon Acanthium</i> L.
210	<i>Sal Tanacetum</i>	<i>Tanacetum balsamita</i> L.
212	<i>Sal Nasturtium aquaticum</i>	<i>Sisymbrium nasturtium-aquaticum</i> L.
214	<i>Sal Theriacalis</i>	From theriaca drug
215	<i>Sal Fragorum</i>	From aromatics compounds
217	<i>Sal Fabarum</i>	From Fabaceae family
221	<i>Sal Pimpinella</i>	<i>Pimpinella anisum</i> L. <i>Pimpinella lutea</i> L. <i>Pimpinella saxifraga</i> L. <i>Sanguisorba minor</i> Scop.

antiseptic and prevents the growth of bacteria. Jarosite was used as a yellow pigment since Middle Paleolithic (of Iberia) corresponding to 50 000 years B.P. (Zilhão *et al.*, 2010). It is important to point out that jarosite in association with goethite is called “Pulvis Astringent” (Astringent powder; sample 203), indicating its possible use in pharmacology. On the other hand, jarosite was used as a cosmetic (and pigment) in the Roman world (Ambers, 2004; Gamberini *et al.*, 2008).

Several species of chlorides (Na, K, Hg, and NH<sub>4</sub>) were detected and among these the most interesting is calomel, a poisonous purgative.

Carbonates – both calcium and lead – and phosphates were commonly used as white pigments. Evidence of calcite and aragonite (shell white) use can be found, for example, as raw materials in Pompeian paintings (Mazzocchin *et al.*, 2006; Giachi *et al.*, 2009) whilst hydrocerussite (and cerussite), known as lead white, are the most important white pigment mentioned from ancient times to the present (Gettens *et al.*, 1993a), also used as a cosmetic. Analyses on 3000–5000 years old cosmetics of Ancient Egypt indicate that cerussite is the principal white component (Dooryhée *et al.*, 2004). Furthermore, the physicochemical analyses of Roman cosmetics from Pompeii revealed that the white powder is principally calcite and gypsum, sometimes cerussite and aragonite (white shell). Calcite was described as a foundation, and it is more common than the lead carbonate (*cerussa*), rare in analysed samples from the Roman period, but often mentioned in the literature. The pink make-up was a mixture of several

products, often hematite (ochre) lightened with a white pigment (often calcite; Welcomme *et al.*, 2006).

Hydroxylapatite, known as bone white, was used since Prehistoric times (Henshilwood *et al.*, 2011). It is important to point out that the corresponding sample 138 was incorrectly labelled calomel.

Tintalconite, a pseudomorph of borax [Na<sub>2</sub>(B<sub>4</sub>O<sub>7</sub>)•10H<sub>2</sub>O], belongs to the borate group used as a flux in cobalt ore processing for blue pigment manufacture process (Matin and Pollard, 2017), and more in general in melting processes. Moreover, the use of boric acid (after dissolution of borates in water) is well known for its antiseptic properties and eye salves; recent applications as antibacterial agent are very promising (Photos-Jones *et al.*, 2015). Finally, it was also an alchemical compound (Testi, 1980).

Among the Mn-oxides possibly used since Prehistory (Chalmin, 2003), bixbyite is a black pigment obtained after heat treatment. The use of cassiterite is not reported elsewhere.

Sulphides are in the form of cinnabar, a red pigment well known to Romans but also in Greece at least since 6<sup>th</sup> century B.C. (Gettens *et al.*, 1993b). Notwithstanding, mercury is a well-known toxic heavy metal, cinnabar has been used for 2000 years in traditional Chinese and Indian Ayurvedic medicine (Liu *et al.*, 2008).

Hematite, beside its use since Prehistory as a pigment and other utilitarian and not utilitarian applications (Cavallo, 2016), was maybe the first mineral medicine used by early human beings (Velo, 1984).

The yellow pigment litharge was used since antiquity (Burgio *et al.*, 2001).

Finally, the composition of *Pietra divina* (Divine stone, sample 98) matches very well that reported in Testi (1980).

## V. CONCLUSIONS

The analysis reported in this study allowed for a clear identification of the inorganic materials stored at the pharmacy *Santa Maria della Scala* in Rome.

It is evident that the pharmacy sold medicines (or principles for medicines), artistic materials, and also products for pigment manufacture (alum-K or borate). This was very common in Italy before the 15<sup>th</sup> century when a specific profession called *vendecolori* (sellers of pigments) was established in Venice that become the most important centre where artists and agents could get artistic materials (Matthew and Berrie, 2010). Similarly, in German-speaking area, artists' pigments were available at pharmacies during the Middle Ages (Burmester *et al.*, 2010). However, the abundance of sulphates and other salts such as chlorides indicates that the commerce of artistic material was not the primary practice in the pharmacy.

The minerals here identified generally occur as individual phases. QPA allowed for the determination of the amount of each component in the polycrystalline mixtures.

There are several aspects that require additional in-depth considerations. First, the salt arcanite is referred to with different (71) names, probably as it is used like a substrate for essences of plants but the following questions remain still open: where did the minerals come from? Did it come from natural or artificial sources? Was the pharmacy a supplier for other pharmacies in Italy or did it purchase mineral pigments from other pharmacies? These and other questions will be the subject of further investigations, where complementary analyses and historical information will be achieved for a more in-depth understanding of the social-economic and trade activities occurring in the preindustrial Mediterranean environment, also including the research on precious stones.

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