



Identity and purity of historical remains of inorganic pharmaceuticals from the eighteenth century

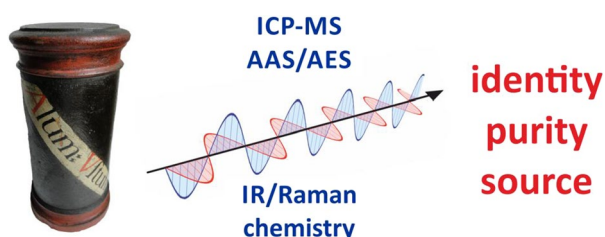
Karel Nesměrák¹ · Eva Janoušková¹ · Václav Červený¹ · Jakub Hraníček¹ · Alice Šimonová¹ · Jana Kunešová² · Ivan Němec³

Received: 12 May 2023 / Accepted: 6 June 2023 / Published online: 23 June 2023
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Abstract

Sixteen specimens of historical remains of inorganic pharmaceuticals dating back to the eighteenth century were analyzed by a combination of spectroscopy (ICP–MS, atomic absorption/emission, UV–Vis, infrared and Raman), capillary zone electrophoresis, and chemical methods (titration and gravimetric analysis). The results obtained confirmed the identity of 14 of the specimens analyzed. With the exception of one, impurities were found in all specimens, often at relatively high concentrations. Based on these impurities, it was possible to confirm the origin of six substances as naturally occurring minerals. The other specimens were probably prepared by period apothecaries or artisans through chemical reactions. In two specimens, a recipe of the time, based on the ignition of metal with sulfur, could be confirmed. For *anatron*, a substance that originated as a by-product of glass melting, it was possible to determine its composition as a mixture of alkaline sulfates, carbonates, and chlorides (the first such analysis described in the literature). On the other hand, for two specimens, it was found that the substance was mistaken for a completely different compound than would be expected from the Latin inscription on the apothecary jar.

Graphical abstract



Keywords Alchemy · Authenticity · Drugs · History of pharmacy · Medical formulations · Minerals

Introduction

The identity of a substance and its purity are a key factor in chemistry. After all, a chemical substance is defined as a form of matter having constant and definite composition best characterized by the entities (molecules, formula units, atoms) it is composed of [1]. Uncertainty in the identity of a substance or its confusion with another can lead not only to the failure of an expected chemical reaction but also to an accident or disaster.

Both identity and purity of a substance play a very crucial role in pharmacy, where confusion of a drug or the mere

✉ Karel Nesměrák
nesmerak@natur.cuni.cz

¹ Department of Analytical Chemistry, Faculty of Science, Charles University, Prague, Czech Republic

² Department of Older Czech History, Historical Museum, National Museum, Prague, Czech Republic

³ Department of Inorganic Chemistry, Faculty of Science, Charles University, Prague, Czech Republic

impurity contained in it (even in very small quantities) can have fatal consequences, in extreme cases even death. While today, the identity and purity of substances used in pharmacy are strictly prescribed by the pharmacopoeia and carefully controlled, this was certainly not the case in the past. Therefore, as part of our project of analyzing the historical remains of pharmaceuticals, we have studied the identity and purity of sixteen inorganic pharmaceuticals from the eighteenth century. The samples analyzed were obtained from the exceptionally preserved Baroque pharmacy of the Capuchin monastery in Prague at Hradčany (now in the collections of the National Museum in Prague) [2]. Thanks to a remarkable coincidence, the remains of pharmaceuticals from this pharmacy have been untouched by human hands since the end of the eighteenth century. In our previous works, we have studied preparations containing herbal substances from this pharmacy; for example, chicory extract [3], senna extract [4], preparations containing opium [5, 6] or ipecacuanha [7] and baroque ointments [8].

The analysis of historical remains of inorganic pharmaceuticals has been discussed several times in the literature; we give an overview of such analyzes in our review [9]. Vázquez de Ágredos Pascual et al. [10, 11] recently analyzed several dozen inorganic compounds from the nineteenth century pharmacy of Santa Maria della Scala in Rome. In the past, a number of inorganic drugs were also used by alchemists [12]. In fact, iatrochemistry, which in turn applied alchemical ideas and working practices to the production of medicines, emerged from this milieu. An eminent example of the analysis of iatrochemical medicine is Principe's work [13], in which, based on a replication of an alchemical procedure of the time, he demonstrated that the impurities contained in the mineral raw materials used in the production of a medicine can significantly affect the outcome of the preparation of such a medicine.

An overview of the historical remains of inorganic pharmaceuticals analyzed in this work is presented in Fig. 1 and Table 1.

Results

Elemental composition in samples analyzed

To determine the elemental composition of the historical remains of inorganic pharmaceuticals analyzed, their solutions in 2% nitric acid were used. Samples that did not completely dissolve in this medium were dissolved in aqua regia (that is, samples H2-4765, H2-4773, H2-4817, H2-4819, H2-4851, H2-4857, and H-9507). The elemental composition was determined by inductively coupled plasma mass spectrometry (ICP-MS) as the main method. The content of elements present at higher concentrations (more than 1%)



Fig. 1 Baroque apothecary jars from which samples were taken for analysis (inventory number in the collection of the National Museum, transcription of the Latin inscription on the jar) **a** H2-4714 *Vitriolum album*, **b** H2-4763 *Alumen crudum*, **c** H2-4765 *Chalybs limatura*, **d** H2-4773 *Plumbum ustum*, **e** H2-4794 *Nihilum album*, **f** H2-4802 *Anatron*, **g** H2-4817 *Chalybs Martis*, **h** H2-4819 *Aes viride*, **i** H2-4836 *Alumen ustum*, **j** H2-4851 *Chalybs cum sulphure praeparatio*, **k** H2-4857 *Lapis calaminaris*, **l** H2-4902 *Vitriolum Martis calcinatum*, **m** H2-9507 *Viride cupri*, **n** H2-9543 *Saccharum Saturni*, **o** H2-9582 *Nitrum depuratum*, **p** H2-9643 *Borax veneta* (Color figure online)

was simultaneously determined and confirmed by atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES), ultraviolet–visible (UV/Vis) spectroscopy, or titration. The quantification of the elemental content of the samples analyzed is presented in Table 1, which also gives the theoretical composition based on the Latin inscription on the apothecary jar from which the sample originated. According to the detected concentrations, the elements were divided into (i) macroelements, which were considered to be elements present in concentrations greater than 1%, these elements forming a major component of the sample analyzed or its significant impurity, and (ii) microelements, that is, elements present in concentrations less than 1%, which can, therefore, be considered as impurities.

Quantification of anions in samples analyzed

For the historical remains of inorganic pharmaceuticals analyzed, which were expected to have significantly represented

Table 1 Elemental composition of the historical remains of inorganic pharmaceuticals analyzed (inventory number; theoretical composition without hydrate water; macroelements, i.e. elements represented > 1%; microelements, i.e. elements represented < 1%)

Inv. no	Theoretical composition	Macroelements/%	Microelements/%
H2-4714	ZnSO ₄	Zn 16.8; Fe 3.80; Mn 2.14	Mg 0.24; Cu 0.21; K 0.17; Na 0.09; Cd 0.05
H2-4763	KAl(SO ₄) ₂	Al 5.56	Fe 0.11; Ca 0.10; K 0.14; Na 0.005
H2-4765	Fe	Fe 74.7	Cu 1.00; Zn 0.35; P 0.18
H2-4773	PbS	Pb 86.0; Sb 1.04	Sn 0.60; As 0.44; Cu 0.40; Fe 0.09; Ca 0.08
H2-4794	ZnO	K 32.7; Ca 4.30	Rb 0.29; Na 0.32; As 0.0012
H2-4802	Mixture of K ₂ SO ₄ , K ₂ CO ₃ and KCl	K 49.3	Ca 1.57; Na 0.66; Rb 0.06; Ba 0.06
H2-4817	Fe	Fe 41.2	Ca 0.74; Al 0.28; Mg 0.10
H2-4819	Cu salt	Cu 46.9; Pb 2.00; Ca 1.05	Al 0.12; As 0.10; Fe 0.09; Ni 0.08; Sb 0.07
H2-4836	KAl(SO ₄) ₂	Al 6.33	K 0.72; Na 0.03
H2-4851	FeS	Fe 46.3	Mn 0.05
H2-4857	ZnCO ₃	Ca 19.6; Mg 12.3; Zn 3.73; Fe 1.23	Pb 0.29; Mn 0.11; Al 0.09
H2-4902	FeSO ₄	Fe 21.4; Cu 1.40	Mg 0.46; Zn 0.26; Ca 0.16; K 0.04; Na 0.02
H2-9507	Cu salt	Cu 49.8	Ca 0.14; Sb 0.14; As 0.11; Mg 0.02; Fe 0.005
H2-9543	Pb(CH ₃ COO) ₂	Pb 65.7	None
H2-9582	KNO ₃	K 37.7	Na 0.04
H2-9643	Na ₂ B ₄ O ₇	K 18.6; Na 16.0	Ca 0.15

The relative standard deviation of all values is < 10%

anions, quantification of these anions in aqueous sample solutions was performed by capillary zone electrophoresis. The exception was sample H2-4773, which was dissolved in aqua regia, for which it could be expected that the sulfide anion present in the sample would be oxidized to sulfate anion by aqua regia. The sample H2-9643 was subjected to simultaneous determination of the borate anion by acidimetric titration. The results obtained are presented in Table 2.

Infrared and Raman spectroscopy of samples analyzed

The nature of the selected specimens of the historical remains of inorganic pharmaceuticals analyzed was

investigated by FT-IR and Raman spectroscopy. The recorded IR spectra of samples H2-4773 and H2-4817 indicate the presence of at least trace amounts of sulfates. This conclusion is based on the presence of bands of ν_3 SO₄²⁻ modes (wide band at 1080 cm⁻¹ for H2-4817 and asymmetric doublet at 1163 and 1044 cm⁻¹ for H2-4773), ν_1 SO₄²⁻ mode (weak band at 965 cm⁻¹ for H2-4773) and ν_4 SO₄²⁻ modes (asymmetric doublet at 624 and 591 cm⁻¹ for H2-4773).

The Raman spectra of the sample H2-4794, depicted in Fig. 2, clearly show that the main component of the sample is potassium sulfate (characteristic bands at 1145, 1108, 1093, 963, 626, 619 and 455 cm⁻¹). The Raman spectrum of sample H2-4851 (Fig. 3) manifests the presence of elemental

Table 2 Quantification of anions in the historical remains of inorganic pharmaceuticals analyzed (inventory number; theoretical composition without hydrate water; percentage of sulfate, carbonate and other anions)

Inv. no	Theoretical composition	SO ₄ ²⁻ /%	CO ₃ ²⁻ /%	Other anions/%
H2-4714	ZnSO ₄	39.1	3.40	
H2-4763	KAl(SO ₄) ₂	48.4	1.7	
H2-4773	PbS ^a	45.5		
H2-4794	ZnO	45.8		
H2-4802	Mixture of K ₂ SO ₄ , K ₂ CO ₃ and KCl	56.9	3.6	0.41 Cl ⁻ , 0.04 PO ₄ ³⁻
H2-4836	KAl(SO ₄) ₂	48.9	2.0	
H2-4902	FeSO ₄	39.5	6.5	
H2-9543	Pb(CH ₃ COO) ₂			34.6 CH ₃ COO ⁻
H2-9582	KNO ₃	0.40	7.58	62.3 NO ₃ ⁻
H2-9643	Na ₂ B ₄ O ₇	0.20	12.81	75.2 BO ₃ ³⁻

The relative standard deviation of all values < 5%

^aSample was dissolved in aqua regia, so that the sulfur was oxidized to sulfate anion

sulfur S_8 by the characteristic bands at 472, 247, 218 and 153 cm^{-1} (cf. [14]).

The vibrational spectra of the sample H2-4857 exhibit manifestations of carbonate anions with lowered symmetry; i.e., splitted bands of $\nu_3\text{ CO}_3^{2-}$ modes at 1479 and 1418 cm^{-1} (IR spectrum), $\nu_1\text{ CO}_3^{2-}$ mode at 1086 cm^{-1}

(Raman spectrum), $\nu_2\text{ CO}_3^{2-}$ mode at 875 cm^{-1} (IR spectrum) and $\nu_4\text{ CO}_3^{2-}$ mode at 712 cm^{-1} (both spectra). However, the IR spectrum also shows features characteristic to hydroxides (stretching O–H vibrations); i.e., wide structured bands in the region $3500\text{--}2700\text{ cm}^{-1}$ and a sharp peak at 3648 cm^{-1} .

Fig. 2 Raman spectrum of sample H2-4794 *Nihilum album* (red line) compared to the reference spectrum of potassium sulfate (blue line) (Color figure online)

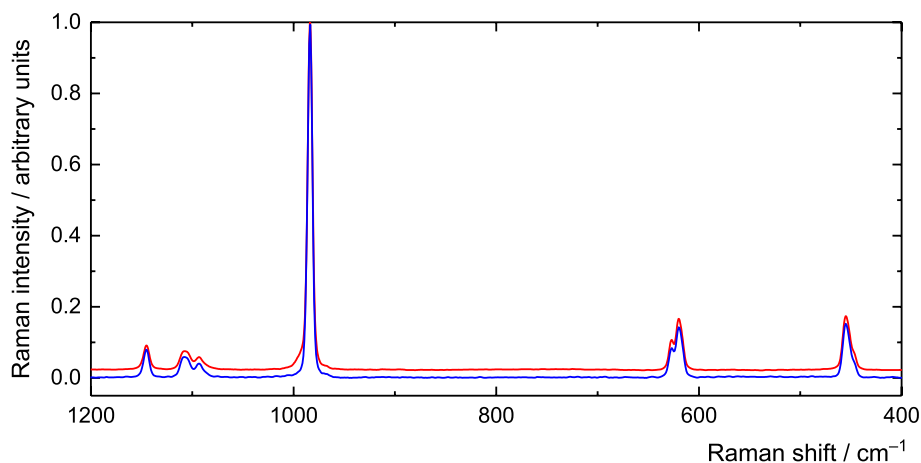


Fig. 3 Raman spectrum of sample H2-4851 *Chalybs cum sulphure praeeparatio* (red line) compared to the reference spectrum of cyclooctasulfur molecule (blue line) (Color figure online)

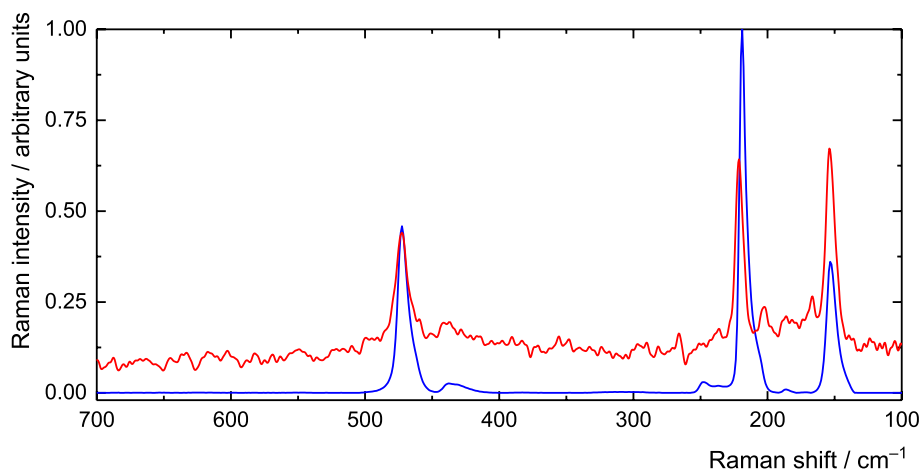
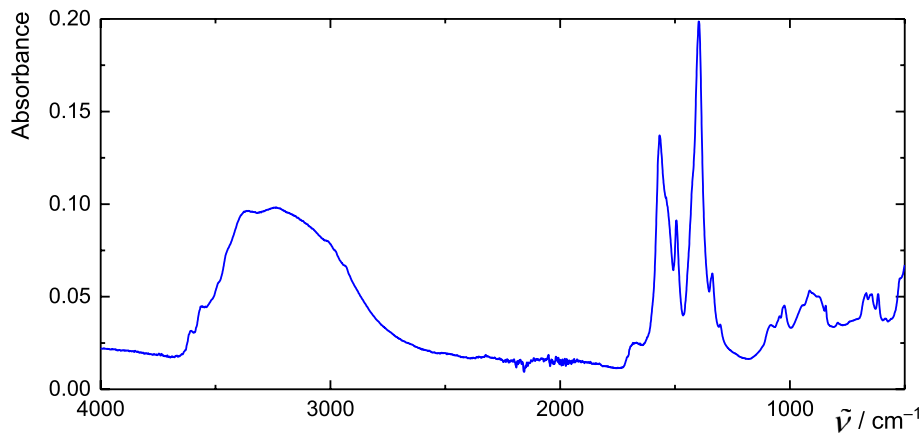


Fig. 4 Infrared spectrum of sample H2-9507 *Viride cupri*



The recorded IR spectra of the sample H2-9507 (Fig. 4) show that this is an acetate-type verdigris [15, 16]. The comparison with the reference spectrum [17] of synthetic verdigris (composition $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{Cu}(\text{OH})_2$) clearly indicates the close relationship of the spectra. The spectrum of sample H2-9507 contains a broad band of stretching O–H vibrations (maximum at $\sim 3200 \text{ cm}^{-1}$) and a pair of strong bands at 1567 and 1397 cm^{-1} belonging to antisymmetric and symmetric COO^- vibrations, respectively. The increased relative intensity of the band at 1397 cm^{-1} and the presence of a sharp band at 1494 cm^{-1} also indicate the presence of carbonate anions (splitted bands of $\nu_3 \text{CO}_3^{2-}$ modes) in the sample.

Solubility and waters of hydration of the samples analyzed

Two specimens of historical remains of inorganic pharmaceuticals analyzed, which according to the theoretical or established composition should be well soluble in water, were found to contain a water-insoluble fraction. This fraction was quantified gravimetrically; for sample H2-4794 the water-insoluble fraction was determined to be 2.66%, for sample H2-4802 the water-insoluble fraction was determined to be 2.23%.

For three specimens analyzed, the content of hydrate water was determined by gravimetric method, and the results of the determinations are summarized in Table 3.

Discussion

The historical remains of inorganic pharmaceuticals analyzed in this work can generally be broadly divided according to their composition determined into (i) raw materials of natural origin, that is, minerals obtained by collecting or mining, and (ii) substances prepared by chemical reactions. Classification into the first group is usually sanctioned by the higher impurity content of the analyzed pharmaceutical. The apothecaries of the time did not, of course, analyze such substances of natural origin, but accepted their identity as given solely on the basis of the origin of the substance (declared by

the supplier) or on the basis of characteristic features such as consistency, color, or solubility. This could easily lead to confusion. This is the reason why the two samples analyzed from the study set, H2-4794 and H2-4857, were mistaken by a period apothecary for a substance completely different than the Latin inscription on the apothecary jar suggests. Next, the theoretical and determined composition of the analyzed historical remains of inorganic pharmaceuticals is discussed, set in a brief pharmaceutical-historical context. The analyzed samples are grouped alphabetically according to the content of the main element.

Aluminium

Sample H2-4763 and similar sample H2-4836 were confirmed as aluminium potassium sulfate (trivially called “alum”), used in the eighteenth century to treat scurvy, as a scar remover and as a component of topical preparations [18, 19]. A higher aluminium content was found in sample H2-4836, which is consistent with the Latin inscription on the apothecary jar *Alumen ustum*, suggesting that it is ignited alum (ignition reduces the hydrate water content) [19]. The impurities present indicate that the source of both specimens analyzed was a mineral, probably alunite [20], which was, therefore, used as either raw (sample H2-4763) or ignited (sample H2-4836).

Boron

Of the samples in the studied set, the specimen with boron content was represented in only one case. For this sample H2-9643, its identity as an alkaline tetraborate (trivially called “borax”) was confirmed by analysis, consistent with the Latin inscription on the apothecary jar. The sample is a mixture of hydrated sodium tetraborate and potassium tetraborate, with admixtures of both sodium/potassium carbonate and sodium/potassium sulfate. Borax was usually obtained as a mineral from various natural deposits and then purified (especially in Venice, hence the name of the substance *Borax veneta*) by crystallization [20, 21]. It was used as an abortive, diuretic, and in preparations for the treatment of arthritis and female disease [18, 19].

Copper

The Latin inscription *Aes viride* on the apothecary jar of sample H2-4819 suggests that it is the copper salts of acetic acid, also known by the trivial name “verdigris”. It has been used for centuries as a pigment in painting [15, 16], and has had an equally important place in pharmacy, where it was applied as a disinfectant in topical preparations since the time of ancient Egypt [19, 21]. It was prepared by dissolving copper compounds (oxide, carbonate) in acetic acid by

Table 3 Quantification of hydrate water in selected historical remains of inorganic pharmaceuticals determined by ignition of the sample at $350 \text{ }^\circ\text{C}$ (inventory number; theoretical composition without hydrate water; percentage of hydrate water determined)

Inv. no	Theoretical composition	Water content/%
H2-4714	ZnSO_4	35.2
H2-4902	FeSO_4	29.1
H2-9643	$\text{Na}_2\text{B}_4\text{O}_7$	34.5

The relative standard deviation of all values $< 2\%$

various methods. The analysis of the specimen confirmed the high copper content of the sample, but due to the small amount of preserved sample, further characterization by spectroscopy was not possible. On the contrary, for the second copper-bearing historical remains analyzed, sample H2-9507, it was possible not only to determine the high copper content but also to confirm by IR spectroscopy that this specimen is indeed acetate-type verdigris.

Iron

There were four samples with iron as the main component. In sample H2-4765, a high iron content corresponding to a mixture of its oxides was found. The substance was prepared by sawing metallic iron, hence the literal translation of the Latin inscription *Chalybs limatura* on the apothecary jar “sawed iron”. It was used in preparations for liver disease and anemia [19, 21]. The action of air oxygen naturally oxidized such iron filings over the centuries. Schröder found similar content in another historical relic of *Chalybs limatura* dated to the seventeenth century [22]. Practically the same conclusions were found for sample H2-4817 *Chalybs Martis* (literally “the iron of the god Mars”). Again, this is a mixture of iron oxides and iron oxide-hydroxides, moreover in a mixture with sulfate, as shown by the IR spectra. In the third sample analyzed, H2-4851 *Chalybs cum sulphure praeeparatio*, ferrous sulfide was confirmed. It was produced by calcination of iron with sulfur and was used as an astringent, roborant, and antacid [18, 19]. Compared to the theoretical composition, only 72% FeS was found in the sample, this is probably the result of an incomplete reaction during preparation; the rest of the sample consists of unreacted sulfur and impurities. This is confirmed by the presence of elementary sulfur in the sample as detected by Raman spectroscopy. Analysis of a fourth iron-containing sample, H2-4902, confirmed the presence of ferrous sulfate (trivially called green vitriol). The compound was used in the eighteenth century pharmacy to treat tuberculosis and to produce bleeding-stopping agents [19, 21]. According to the Latin inscription *Vitriolum Martis calcinatum* on the apothecary jar, it is supposed to be ferrous sulfate calcined. However, the iron content found corresponds roughly to that in ferrous sulfate heptahydrate. In addition, the sample contains a small proportion of sulfates and carbonates impurities, particularly copper and zinc. The source of the substance could have been either a mineral (especially melanterite or rozenite [20]) or the chemical reaction of iron or its compounds (oxides) with sulfuric acid.

Lead

The first sample analyzed, H2-4773, bears the Latin name *Plumbum ustum*, literally “burnt lead”. According to the

historical literature [18, 19], this substance was prepared by placing lead sheets in a crucible together with sulfur and by strong ignition a brown powder was obtained. Lead sulfide was thus formed, and it was used in preparations for skin diseases, scar healing, and hemorrhoids. This corresponds to an observed lead content of 86%; the theoretical lead content in lead sulfide is 86.6%. After dissolution of the sample in aqua regia for analysis, the sulfur of the sulfide anion was oxidized to sulfates, of which 45.5% was found (i.e., 113% of the theory). The use of sulfur in the preparation of this specimen is also evidenced by the traces of sulfate demonstrated by IR spectroscopy. The metallic impurities found (mainly antimony and arsenic) come from the ore used in the production of lead. The second historical lead-bearing sample analyzed, H2-9543, was confirmed to be pure lead acetate. The substance, known since antiquity for its sweet taste (hence the Latin name *Saccharum Saturni*, literally “Sugar of Saturn”), was prepared by dissolving lead or its compounds in acetic acid [19, 22]. Schröder [22] analyzed a sample from the nineteenth century and obtained a similar result.

Potassium

There were two potassium salts in the study set. An interesting substance used in the eighteenth century pharmacy was *anatron* (also called *Fel vitri*, literally “bile of glass”), a by-product of glass melting [19]. It was used mainly for its diuretic effect [21]. The identity of sample H2-4802 was confirmed and it was found that the sample contains alkaline sulfates (56.9%), carbonates (3.6%) and chlorides (0.41%). The water-insoluble fraction of 2.23% corresponds to the sulfates and carbonates of barium and calcium present. To the best of our knowledge, this is the first analysis of *anatron* described in the literature. The second potassium salt in the study set was sample H2-9582. In accordance with the Latin inscription on the apothecary jar *Nitrum depuratum*, the analysis confirmed the specimen composition as potassium nitrate with minor admixtures of alkaline carbonates and sulfates. It was obtained by purifying of the mineral niter [20] (hence *depuratus*, literally “purified”) or artificially prepared from organic residues [19, 21]. In the pharmacy of that time, it was used in anti-inflammatory preparations and as a digestant.

Zinc

Analysis of sample H2-4714 *Vitriolum album* confirmed that it is indeed zinc sulfate (trivially called “white vitriol”). In the eighteenth century pharmacy, it was used mainly as an emetic, as part of eye drops or topical preparations [18, 19, 22]. However, the specimen analyzed is not pure zinc sulfate, but a mixture of 74% $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 16% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 7% $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$ and 3% other admixtures

(calculated based on the results of analyzes). This composition corresponds to the mineral goslarite [20], which was a natural source of zinc sulfate in the eighteenth century. The second specimen that was believed to contain a zinc compound was sample H2-4794. The Latin inscription on the apothecary jar *Nihilum album* (literally “white nothing”, or “white snow”) has been used for centuries for zinc oxide [19, 21]. It was available in nature as the mineral zincite [19, 20], but more often it was prepared synthetically as a by-product of the metallurgical processing of zinc ores. Zinc oxide was mainly used in topical preparations. However, the results of analyzes showed that in this case it is a completely different substance, which does not contain zinc at all. It is a mixture containing 73% K_2SO_4 , 11% $CaCO_3$ and 16% other admixtures (calculated based on the results of analyzes). It is the presence of calcium carbonate (which is poorly soluble in water) that can create the illusion that it is zinc oxide, which is also insoluble in water (if by chance the apothecary of the time tested the solubility of the substance in water). This is proven by the determination of the water-insoluble fraction, which is 2.66%. The third zinc-containing specimen was sample H2-4857, which according to Latin inscription on apothecary jar *Lapis calaminaris* should be mineral calamine (synonymously smithsonite, chemically zinc carbonate [20]). The substance, as the aforementioned zinc compounds, was used mainly in topical preparations [19, 21]. However, the analysis of the specimen shown that—also in this case—it was mistaken for another substance. Based on the results of the analysis, the composition of the specimen can be characterized as 48.9% $CaCO_3$, 42.7% $MgCO_3$ and 7.2% $ZnCO_3$, the remaining 1.2% being other admixtures. Therefore, it is definitely not calamine, which contains 80.3% zinc, but most probably mineral dolomite [20].

Conclusions

The combination of several spectral techniques, capillary zone electrophoresis, and classical chemical methods of analysis provided an interesting insight into the pharmaceutical and artisanal practice of the eighteenth century with possible overlap into alchemy. In the studied set of 16 historical remains of inorganic pharmaceuticals, the identity of the main constituent was confirmed in 14 cases. In two cases, however, it turned out that period apothecaries or their suppliers had mistakenly replaced the alleged substance with a chemically completely different one. In all, except for one, numerous impurities were found in the specimens studied. Based on these impurities, it was possible to estimate the mineral sources of the substance in six cases. Analysis of two specimens allowed us to confirm a recipe of the time,

which consisted of synthesis from metal and sulfur by ignition. For the first time, *anatron*, a substance commonly used in the eighteenth century pharmacy, was analyzed.

Experimental

Analyzed samples, chemicals

The historical remains of inorganic pharmaceuticals analyzed were collected directly from the original Baroque apothecary jars. The inventory numbers of the individual jars in the collection of the Department of Older Czech History, National Museum (Prague, Czech Republic) are given in Table 1. The appearance of the jars is specified in Fig. 1. Eleven jars were hollowed out of wood in the shape of a cylinder 140 mm high and 90 mm in diameter. The five vessels were in the shape of a glass cup 120–150 mm high and 50–70 mm in diameter, which was closed with an original leather lid secured with a string. After carefully opening the jar, three samples of the contents were taken from the jar using a porcelain spoon (one from the center and two from opposite sides). The exception was sample H2-4819, where only a small amount of residue was recovered from the vessel. The samples were kept in glass containers in the dark and homogenized in a porcelain mortar prior to analysis.

All of the chemicals used were of p.a. grade or higher. Deionized water, prepared on a Milli-Q instrument (Millipore, USA), with a specific conductivity $< 0.05 \mu S cm^{-1}$, was used.

Procedures, instrumentation

The ICP-MS measurements were performed on an Inductively Coupled Plasma Mass Spectrometer ICP-MS 7900 (Agilent, USA) equipped with a micromist glass nebulizer working at 1550 W (with a flow 1.03, 0.90, and $15.0 dm^3 min^{-1}$ of nebulizer, auxiliary and plasma gas, respectively). Results were evaluated from the “No gas” mode. For calibration and sample solutions preparation, 2% (v/v) nitric acid was used. In the case of samples dissolved in aqua regia, the resulting solution was diluted by water so that the resulting nitric acid concentration was below 2%. Working standards were prepared by an appropriate diluting of two multielement certified reference solutions (i) AN9094MFN CRM Mix (As, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn) with concentration of $100 mg dm^{-3}$ of each element in 5% HNO_3 and 0.2% HF (Analytika, Czech Republic), and (ii) AN9087MC (Au, Ir, Os, Pd, Pt, Rh, Ru) with concentration of $100 mg dm^{-3}$ of each element in 20% HCl (Analytika, Czech Republic). The concentrations

of all elements in the calibration solutions were in a concentration range of 1.6–1000 $\mu\text{g dm}^{-3}$.

The High Resolution Continuum Source Atomic Absorption Spectrometer ContraAA700 (Analytik Jena, Germany) was used for the determination of Al, As, Ca, Cd, Fe, K, Mg, Na, Pb, and Zn using an external calibration approach. All calibration solutions were prepared from certified reference materials (Analytika, Czech Republic) with a concentration of determined element (1000 ± 2) mg dm^{-3} . The samples and standards were diluted with 1% HCl or HNO₃. For all measurements, 0.1% CsCl ionization buffer was used. Calcium, potassium, and sodium were determined in the atomic emission mode, and all other elements were determined in the atomic absorption arrangement. Only three pixels (central pixel ± 1 side pixel from the 200 observed) were used for the signal evaluation. In case of self-absorption observed, the sample was diluted as needed to avoid this unfavorable phenomenon. The wavelengths and other experimental conditions for the determination of individual elements are summarized in Table 4.

UV/Vis spectrometry was carried out on a single-beam diode array spectrometer HP-8453 (Agilent, USA) in a quartz cuvette with an absorption layer thickness of 1 cm. The 1,10-phenanthroline method was used for the determination of iron [24], and the aqueous ammonia method was used for the determination of copper [25].

For the chelatometric determination of the lead content, exactly about 0.05 g of the sample was weighed, diluted in a titration flask with 100 cm^3 of deionized water and 3 g of hexamethylenetetramine were added. The resulting solution was titrated with 0.05 mol dm^{-3} volumetric solution of

EDTA. Xylenol orange was used to indicate the equivalence point.

Electrophoretic measurements were carried out on an Agilent 7100 capillary electrophoresis instrument (Agilent Technologies, Germany) equipped with a capacitively coupled contactless conductivity detector (Admet, Czech Republic). The measurement temperature was maintained at 25 °C. A fused-silica capillary (Polymicro Technologies, USA) of 20 μm i.d., 375 μm o.d. was cut to 50.0 cm total length, 35.0 cm effective length. Prior to the first use, the capillary was flushed 10 min with 1.0 mol dm^{-3} aqueous solution of sodium hydroxide and then 10 min with deionized water. Between individual runs, the capillary was flushed 5 min with the background electrolyte. The sample was introduced by a pressure of 5 kPa for 20 s. The determination of chloride, sulfate, nitrate, and phosphate was carried out in a background electrolyte consisting of 1.0 mol dm^{-3} aqueous solution of formic acid. During separation, the voltage was set at -25 kV (current was 8 μA). Quantification was based on a 7-point calibration curve with standards ranging from 0.05 to 5.00 mmol dm^{-3} concentration. Peak areas were related to the peak area of benzene-sulfonate, added as an internal standard at a concentration of 1 mmol dm^{-3} . The determination of carbonate, acetate, and borate ions was carried out in a background electrolyte consisting of an aqueous solution of 50 mmol dm^{-3} sodium hydroxide, 22.5 mmol dm^{-3} disodium phosphate, and 0.2 mmol dm^{-3} cetyltrimethylammonium bromide. During separation, the voltage was set at -15 kV (current was 9 μA) and a pressure of 100 mbar was applied to the inlet vial. Quantification was based on a 7-point calibration curve with standards ranging from 0.05 to 5.00 mmol dm^{-3} concentration. Peak areas were related to the peak area of 2-(*N*-morpholino)ethanesulfonic acid, added as an internal standard at a concentration of 5 mmol dm^{-3} .

For the acidimetric determination of the borates, exactly about 0.1 g of the sample was weighed and titrated with a 0.1 mol dm^{-3} volumetric solution of hydrochloric acid. The equivalence point was indicated by methyl red.

Infrared spectra were recorded on a Thermo Fisher Scientific Nicolet iS50 FTIR spectrometer (4 cm^{-1} resolution, Happ–Genzel apodization) in the 400–4000 cm^{-1} region (KBr beamsplitter) using the ATR (diamond crystal) technique. Standard ATR correction (Thermo Nicolet Omnic software, version 9.2.89) was applied to the recorded spectra. Raman spectra were recorded on a Thermo Nicolet 6700 FTIR spectrometer equipped with the Nicolet Nexus FT Raman module (4 cm^{-1} resolution, Happ–Genzel apodization, CaF₂ beamsplitter, 1064 nm Nd:YVO₄ laser excitation, 400 mW power at the sample) in the 100–3700 cm^{-1} region.

The water-insoluble fraction was determined by weighing exactly about 0.5 g of the sample in a volumetric flask of 50.00 cm^3 . The flask was filled to the mark with deionized

Table 4 Parameters of determination of individual elements by atomic absorption/emission spectroscopy

Element	λ/nm	Measurement mode
Al	396.1520	AAS: Air/C ₂ H ₂ flame
As	193.696	AAS: Chemical hydride generation with NaBH ₄ in flow injection mode ^a
Ca	422.6728	AES: Air/C ₂ H ₂ flame
Cd	228.8018	AAS: N ₂ O/C ₂ H ₂ flame
Fe	248.327	AAS: N ₂ O/C ₂ H ₂ flame
K	766.4908	AES: Air/C ₂ H ₂ flame
Mg	285.2125	AAS: N ₂ O/C ₂ H ₂ flame
Na	588.995	AES: Air/C ₂ H ₂ flame
Pb	217.0005	AAS: N ₂ O/C ₂ H ₂ flame
Zn	213.857	AAS: N ₂ O/C ₂ H ₂ flame

^aOnly As(III) is convertible to volatile hydride, which can be atomized at 950 °C and determined. Therefore, if the sample contained As(V), for which this atomization method cannot be used, the actual arsenic content would be higher [23]

water and left to stand for 24 h with occasional shaking. The insoluble fraction was determined by filtration through a filter cup (previously dried to constant weight) and subsequent drying at 105 °C.

The hydrate water content was determined gravimetrically by weighing exactly about 0.25 g of the sample into an ignition crucible (previously ignited to constant weight) and then ignited at 350 °C to constant weight.

All measurements were performed at least three times and were statistically evaluated at a 95% confidence level.

Acknowledgements The financial support by the project Cooperatio Chemistry of Charles University is gratefully acknowledged.

Funding Open access publishing supported by the National Technical Library in Prague. This research was funded by Univerzita Karlova, the project Cooperatio Chemistry.

Data availability The experimental data supporting the findings of this study are available from the corresponding author, K.N., upon reasonable request.

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