Platina in the 18th century: mineralogy of the crude concentrate used in the first modern attempts at refining platinum.

by

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Abstract
A platina sample brought to Spain in the last quarter of the 18th century is nowadays exposed at the National Museum of Natural Sciences in Madrid. It comes from the ancient Mineralogical Museum of the School of Applied Chemistry at the El Turco Street in Madrid and most probably it very likely corresponds to the material used by François Chabaneau for his experiments to purify platinum metal in the late 18th century. The sample is a heavy mineral concentrate comprising Pt-Fe alloys and gold nuggets associated with ilmenite-hematite, chromian spinel, goethite and minor quartz, sphene, rutile, magnetite, hornblende,
garnet, calcite, pyrite, native bismuth and bismite. The Pt-Fe alloys exhibit a characteristic chemistry (81.97-90.75 wt.% Pt and 5.08-10.81 wt.% Fe with minor amounts of Cu, Os, Ir, Ru, Rh and Pd) and mineralogy of solid inclusions (abundant inclusions of Ir alloy as well as Os alloy, laurite-erlichmanite, bowieite tulameenite and undetermined Pt-Pd-Ir-Rh antimonides and tellurides) that are very similar to those Pt-Fe alloys currently mined in western Colombia (the Chocó Department). These features allow us to discuss the provenance of the sample (probably from the proximal or medial reaches of any of the Chocó rivers) and evaluate the suitability of the Chabaneau’s method for purifying platina. Our results show that the method became effective only with platina samples depleted or lacking iridium.

Introduction

Platina is the name given by the miners in the Viceroyalty of New Granada in South America (at present, Colombia and Ecuador) to the raw mineral that appears along with gold in the placer deposits. This material was regarded less valuable than silver and hence it was probably termed with a derogatory diminutive of silver (“plata” in Spanish) “platina”, meaning cheap silver. Nevertheless, this raw material was already known some centuries before Christ by the ancient La Tolita-Tumaco cultures settled at the sea coast along the border of the present day Colombia and Ecuador (Scott, 2011 and references therein). These cultures developed a sophisticated metallurgy combining gold and platinum to create alloys, platinum-coated gold objects, platinum-gold sintered alloys and platinum-gold foil-plated objects (Bergsøe, 1937; Scott, 2011).

The Spanish miners realized the presence of platina during mining activities on alluvial gold deposits in the proximal reach of the San Juan river, probably as early as 1690 (Capitán-Vallvey, 1989). Later, it was recognized in most river courses and nearby terraces of the region between the Cordillera Occidental and the Pacific coast, a region known in Colombia
as the Chocó (probably the Esmeraldas region, currently in Ecuador, was considered part of the Chocó in the 18th century; Codazzi, 2002). Platina and gold have similar specific gravities and in these alluvial deposits, they showed similar grain sizes (McDonald & Hunt, 1982) and occurred mixed in different proportions. This prevented efficient separation by panning and consequently, the obtained gold concentrates were found to contain always variable amounts of platina. The much higher melting point of platina relative to gold should lead to its detection in gold concentrates by employees and officials of the local foundries and Royal Mints. These difficulties to identify and separate platina from gold soon aimed miners to deliberately adulterate gold by addition of platina, leading the colonial authorities to ban mining operations in those deposits containing high amounts of platina. Such prohibition remained in force until 1726 when the use of the amalgamation method to separate platina from gold (and at lesser extent the inquartation and melting methods) widens in the region (Capitán-Vallvey, 1988 and 1989). After this year, mining operations in platina-bearing deposits became again permitted but on the condition that platina had to be removed from gold concentrates a process that had to be covered by the owner of the mine. Since at that time platina was still useless and with bad reputation (e.g. Bowles, 1775), once separated it had to be stored by Royal Officials who were in charge of throwing, from time to time, the accumulated platina back to rivers, preferably to inaccessible gorges, like Bogota river, Cauca river (Leblond, 1785) or the one known as the Platina Gorge, in the Novita province (Capitán-Vallvey, 1988). This act prevented platina recovery for falsification of gold shipments and had to be supervised by a Royal Official and certified by a Public Notary. Nowadays, platina is still thrown back to the river after gold amalgamation in some mining sites of the Santiago River in Ecuador (V. Yucas, pers. com.).

Platina attracted the interest of the European scientific community after the publication of a short paragraph on the exceptional properties of this metallic material by Antonio de Ulloa (1716–1795) in the very widespread book written as a result of the French-Spanish geodesic expedition to the Viceroyalty of New Granada (1736-1744) (Juan and Ulloa, 1748). The
interest of European scholars on platina modified the attitude of Spanish authorities of withdrawing the platina from circulation to the foundation of a real monopoly (Capitán-Vallvey, 1994a and b). One of their first steps was to establish a platina refining process led by Pierre François Chabaneau (1754–1842) aided by Fausto de Elhuyar (1755–1833) who, in partnership with his brother Juan José, was the first to isolate wolfram in 1783 (Chaston, 1980; McDonald & Hunt, 1982). Chabaneau success took place in 1786 when he was able to produce malleable platinum metal after dissolution of platina in aqua regia, precipitation of Pt as (NH₄)₂PtCl₆, releasing of Pt by thermal decomposition and annealing and hammering alternatively. The procedure was kept secret by a Royal order of King Carlos III promulgated in 1787 to ensure the Spanish crown the monopoly of trade and manufacture of platinum (Rumeu de Armas, 1979; Capitán-Vallvey, 1994a and b). The Spanish crown created a laboratory for the purification of platinum in the Hortaleza Street of Madrid, a place known at that time as the Casa de la Platina (Aragón de la Cruz, 1986) where Chabaneau combined the laboratory work with teaching chemistry. Some of the platinum metal produced in this laboratory was used to create in 1788, one of the first known objects made on platinum in Europe, a beautiful chalice that was given to Pope Pius VI by the Spanish King Carlos III as a present (McDonald & Hunt, 1982). A second laboratory mainly oriented to teaching chemistry was created later in the El Turco Street and Chabaneau was moved there as director. The activity of these two laboratories remained active until 1808 when the Napoleonic troops plundered and destroyed them. From 1767 to 1805, 2846.49 kg of rough platina in documented shipments were imported from the Viceroyalty of New Granada (Capitán-Vallvey, 1999) and between 435 and 560 kg of platinum metal were produced in the Casa de la Platina and the El Turco Street laboratories (Chaston, 1980). This period is known as the Platinum Age in Spain (Fages, 1909).

The platinum purified by Chabaneau, although useful to produce ingots and different kinds of utensils (including the above mentioned chalice) was not free of impurities. In fact, it was mentioned in Chabaneau’s life time that the chalice showed an infinity of cracks that were
covered with silver, which was justified “for not lending this metal, like gold and silver, to receive other forms and lighter and more delicate ornaments” (Blasco Negrillo, 1805). Joseph Louis Proust (1754-1826) himself indicated it in one of the many letters he wrote requesting platina: “other pieces of this metal have not been able to come out ... it will undoubtedly have been due to the very palpable defects of porosity, cracks and lack of union between the parts that are seen in these samples” (Proust, 1803).

Whereas gold, mercury, lead, copper and, mainly iron, were efficiently removed from the refined platinum, the observed variations in color of the aqua regia solutions and in malleability pointed to the presence of some additional unknown constituents: the other platinum-group metals (osmium, iridium, ruthenium, rhodium and palladium). They were identified later by William Hyde Wollaston (England, 1766–1828) (he discovered Pd in 1802 and Rh in 1803), Smithson Tennant (England, 1761–1815) (he discovered Ir in 1803 and Os in 1804) and Karl Karlovitch Klaus (Russia, 1796–1864) (he discovered Ru in 1844). The latter did not use platina from the Viceroyalty of New Granada but from the deposits that were discovered shortly before in the Ural Mountains, in Russia.

A platina sample saved from the looting of Napoleonic troops and that is currently preserved in the National Museum of Natural Sciences in Madrid, offer us the opportunity to investigate the mineralogical nature of the platina used by François Chabaneau. In this paper, we present data on the mineralogy and chemistry of a portion of this historical sample, discussing its probable geologic origin by (i) comparison with published mineralogical data of placer deposits from Ecuador and Colombia and (ii) with results obtained from a mineralogical survey performed on platinum nuggets from active mines in the Rio Santiago, in the Esmeraldas province (northwest Ecuador). We also discuss how the mineralogical expression of the different PGE (platinum-group elements) could help us to understand the experimental results performed by Chabaneau.
The platina sample

François Chabaneau returned to France in 1797 to restore his health (Dujarric-Descombes, 2005) but previously he elaborated a detailed inventory of the laboratory stocks in the School of Applied Chemistry of the El Turco Street when delivering the laboratory to its substitute (Chabaneau, 1797). The small amount of platina reported in the inventory of the museum draws attention, in spite of the main use of the laboratory (Gago, 1984). According to Chabaneau’s inventory there were only “two samples of the mineral (platina) and different results of my work with this metal”. The most valuable specimens of the museum were kept safe in the Bank of Spain (its main building was located nearby the El Turco Street) from French troops pillage, where they remained until 1983. Part of this material is placed nowadays on exhibition in the National Museum of Natural Sciences in Madrid. The sample studied here (it currently weighs 64 grams) is one of the two heavy mineral concentrates (containing platina and gold) selected by Chabaneau to be included in the mineralogical museum of the referred School of Applied Chemistry (Fig. 1a).

Analytical methods

A portion of the platina sample was first mounted on a resin block, polished and studied by reflected optical microscopy, followed by modal analysis using QEMSCAN at the Centro de Instrumentación Científica of the University of Granada (Spain). QEMSCAN is an automated mineralogical technique based on scanning electron microscopy with linked energy dispersive spectrometers. Single mineral grains were investigated by environmental scanning electron microscope (ESEM) under back-scattered electron mode (BSE) in the Centro de Instrumentación Científica of the University of Granada (Spain), prior to electron microprobe analysis (EPMA) in the CCiT laboratories of the University of Barcelona (Spain). Mineral identification and mineral assemblage digital maps using QEMSCAN were achieved by acquisition of chemical spectrum at a set interval (1 µm) on a defined mapping area of the sample’s surface. Data were processed later offline by comparison with a mineralogical
database. The low spatial resolution of this technique allowed us to differentiate even exsolution lamellae from their host.

EPMA data were obtained using a JEOL JXA-8230 instrument equipped with five WDS spectrometers, under an excitation voltage of 20 kV and a beam current of 51 nA, with a beam 2-3 µm in diameter. Monitored spectral lines for platinum-group mineral (PGM) analyses were SKα, AsLα, FeKα, CuKα, CoKα, NiKα, OsLα, IrLα, RuLα, RhLα, PtLα and PdLβ. Standards used were FeS₂ (for Fe and S), GaAs (for As), CuFeS₄ and metallic Ni, Co, Os, Ir, Ru, Rh, Pt and Pd. The spectral lines monitored for gold analyses were SKα, FeKα, CuKα, SbLα, SnLα, AgLα, TeLα, AuLα, HgLα and BiLα, and the standards used were FeS₂ (for Fe and S), CuFeS₄, Ag₂Te for Te, HgS and metallic Sb, Sn, Ag, Au and Bi.

**Pt-Fe alloys**

The studied sample is a heavy mineral concentrate (Fig. 1b) made up of flake-like nuggets of Pt-Fe alloys (37.44% of the studied area) and gold (16.61%) with a most frequent grain size ranging from 0.5 to 1 mm Feret diameter. These precious minerals are accompanied by ilmenite (25.62%) frequently intergrown with hematite (3.96%) in the form of exsolution lamellae of the latter, chromian spinel (2.60%), goethite (1.42%), bismite (1.1%), and minor quartz, sphene, rutile, magnetite, hornblende, garnet, calcite, pyrite and native bismuth (each of these minerals represent less than 1% of the whole sample), as well as some few unidentified minerals (Fig. 2).

The composition of Pt-Fe alloys is quite homogeneous showing no core to rim variations and consisting of 81.97 to 90.75 wt.% (63.28-78.99 at.%) Pt and 5.08 to 10.81 wt.% (15.34-29.16 at.%) Fe (Table 1). They also contain variable but minor amounts of Cu (0.15-1.1 wt.%), Os (0.07-3.77 wt.%), Ir (<5.62 wt.%), Rh (<2.26 wt.%), Pd (<2.26 wt.%) and Ru (<0.72 wt%) (Table 1). Total weight of all PGE but Pt in Pt-Fe alloys varies from 0.51 to 8.55 wt.% (0.43-9.63 at.%). These values are comparable to those reported by Cabri et al., (1996) in Pt-Fe
alloys from the Condoto river (Colombia) and by Weiser and Schmidt-Thomé (1993), Yucas (2017), Lopez-Males (2017) and Castiella (2018) from the Santiago river (Ecuador).

As a whole, the composition of the different studied grains shows a nearly bimodal distribution centered mainly at 24-25 at.% Fe+Cu and ~17 at.% Fe+Cu (Fig. 3). In contrast to chemical compositions, the 136 nuggets investigated are heterogeneous in terms of abundance of minerals inclusions. As shown below, they mainly consist of other platinum-group minerals but also contain minor chromian spinel, quartz and gold. The presence of irregular inclusions of native gold in Pt-Fe alloys, like that shown in Fig. 4a, has not been reported before and could constitute a characteristic feature of some Chocó placer deposits.

**Platinum-group minerals**

Around 63% of the studied Pt-Fe nuggets contain iridium inclusions either arranged in an irregular, emulsion-like pattern (the size of individual inclusions ranges from <1 μm to few tens of micrometers) or forming cross-cutting, long (up to 70 μm) but fine (<1 μm) exsolution lamellae oriented crystallographically in the host (Figs 4b,c). The former textural type also includes anhedral to subhedral crystals of iridium. The chemical composition of iridium inclusions shows important amounts of Os, with the Ir/(Ir+Os) ratio ranging from 0.61 to 0.90, and minor Pt (9.22-17.05 wt.%), Rh (3.18-6.27 wt.%) and Ru (0.28-3.31 wt%) (Table 2). Similar inclusions in Pt-Fe alloys were described by Cabri et al., (1996) in the placer deposits of the Condoto River (Colombia). The extreme thinness of the iridium exsolution lamellae made it difficult accurate analysis although some few of them obtained from the intersection of lamellae show compositions very close to those of the emulsion-like inclusions (analysis 43, Table 2).

Some nuggets show the presence of single, variably sized (from 1.13x2.5 μm to 4.17x187.5 μm) lamellae of osmium, but one of them, measuring 0.62x1.48 mm, contains up to 90 lamellae (Fig. 4d). These lamellae were detected and quantified by QEMSCAN showing that
their modal percentage reaches 0.39% of the sample (Fig. 2). They have a rather pure composition, with Os/(Os+Ir+Rh+Ru+Pt) ranging from 0.89 to 0.93 (Table 2).

Four Pt-Fe nuggets contain inclusions of laurite-erlichmanite (RuS₂-OsS₂). They tend to be subhedral with a grain size varying from 6.4x8.6 μm to 35.7x85.7 μm, and appear often highly fractured, especially when the inclusions locate close to grain boundaries or fractures of nuggets. Some of them show oscillatory zoning (in the sense of Gonzalez-Jiménez et al., 2009), generally with Ru-rich nuclei [e.g. (Ru₀.⁴₆Os₀.₄₂Rh₀.₀₈Ir₀.₀₄)Σ=1.₀(S₁.₉₇As₀.₀₂)Σ=1.₉₉] and rims with variably but higher Os contents [up to (Os₀.₇₃Ru₀.₁₅Rh₀.₀₈Ir₀.₀₄)Σ=1.₀₁S₁.₉₈] (Table 2 and Fig. 4e). The composition of unzoned grains (e.g. Fig. 4f) tends to approach that of laurite: (Ru₀.₆₇Os₀.₂₂Rh₀.₀₇Ir₀.₀₄)Σ=1.₀(S₁.₉₆As₀.₀₃)Σ=1.₉₉.

One Pt-Fe alloy grain contains several subidiomorphic, minute (from 5.₉x₁₇.₆ μm to 32.₄x₇₆.₅ μm) inclusions of bowieite (Rh₂S₃) (Fig. 4f). Their composition is quite constant, with an average structural formula Rh₁.₃₈Ir₀.₆₇S₂.₉₈ (Table 2). Another one contains a rounded inclusion of tulameenite (Pt₂FeCu) measuring 26.₈ μm across and showing a nearly stoichiometric formula: Pt₂.₀₁Fe₁.₆Cu₀.₉₉. A third one measuring 200x₆₀₀ μm is partly rimmed by an undetermined Pt and Pd antimonide, containing abundant minute inclusions of Pt-Te and Pt-Ir-Rh-Sb-Te.

Most PGM inclusions identified in the studied sample have been already described in Pt-Fe nuggets from alluvial placer deposits worldwide (Cabri et al., 1996; Weiser, 2002), but the emulsion-like, iridium inclusions described here have previously only been observed in nuggets collected in the sites of Delfin and Nevado, located in the proximal reach of the Condoto river in Colombia (Cabri et al., 1996).

Gold

Almost all gold nuggets are zoned but a large one, measuring 1.₃ mm across shows a complex microintergrowth texture. The zoning pattern is rather similar in all grains consisting
of Ag-rich nuclei surrounded by almost pure gold rims (Fig. 5a). Rims locally contain inclusions of partially chloritized biotite. Ag content in nuclei ranges from 4.02 to 17.66 wt.% (7.21-28.46 at.%), whereas in rims it is always below 1.39 wt.% (2.52 at.%) (Table 3). A similar pattern of zoning has been reported in alluvial gold from several placer deposits in the southeastern United States and interpreted as the result of gold precipitation from the surrounding solutions on preexisting electrum nuggets (Groen et al., 1990). The grain with the intergrowth texture is mainly made up of gold (with <3.06 wt.% Bi) and bismite (Bi$_2$O$_3$), but gold often contains irregular inclusions of native bismuth with up to 3.24 wt.% Au (Fig. 5b; Table 3). This mineral assemblage and texture form by low temperature decomposition of maldonite (Au$_2$Bi) giving rise to intergrown Au and Bi (Okamoto and Massalski, 1983; Zhou et al., 2016), followed by oxidation of Bi, probably at weathering conditions, forming bismite. The native Bi included in gold kept isolated from oxidizing solutions and thus represents proof of the pre-weathering Au-Bi microintergrowth.

**Discussion**

**Origin of the sample**

Tracing the local source of platina imported to Spain in the 18th century could be considered an almost impossible task due to the multitude of platina-bearing rivers in the western region of the Viceroyalty of New Granada and the lack of an efficient commercial structure at that time (Capitán-Vallvey, 1996). However, the mineralogical data obtained from the sample studied here indeed allow to carry out a comparison with published data on similar mineral concentrates recovered from some placer deposits from the Chocó region (Colombia) and the Esmeraldas province (Ecuador). Unfortunately, published mineralogical information exists only from several sites at the proximal and medial reaches of the Condoto River (Cabri et al., 1996), a tributary of the San Juan River (Colombian Chocó), and from the
medial reach of the Santiago River in the Esmeraldas province (Weiser and Schmidt-Thomé, 1993).

As noted above, the composition of Pt-Fe alloys from this historical sample shows two maxima at 24-25 at.% Fe+Cu, as well as some few analyses grouping at ~17 at.% (Fig. 3). The comparison of this distribution with those of Pt-Fe nuggets collected at different sites along the proximal and medial reaches of the Condoto River (Cabri et al., 1996) shows some similarities with the composition of Pt-Fe alloys from the El Paso site (Fig. 6a), located in the medial reach of the river. This figure might suggest that the composition of Pt-Fe alloys from the Condoto River slightly varies in terms of their Fe+Cu contents from the proximal to the medial reaches. This would evidence that the closer the sampling site to the source rocks (in this case, the Alto Condoto Zoned Complex located at the catchment area of the river) the higher the Fe+Cu contents of the alloys. However, this suggested subtle trend cannot be verified since no data from the distal reach of the Condoto River are available.

If the studied Pt-Fe alloys are compared with those from the medial reach of the Santiago River (Weiser and Schmidt-Thomé, 1993), it becomes evident that Pt-Fe alloys from this river are richer in platinum than those of the studied historical sample (Fig. 6b). According to Weiser and Schmidt-Thomé (1993) and the analytical data listed by Cabri et al., (1996), the Fe+Cu contents in the alloys show a bimodal distribution with most nuggets containing 15 to 21 at.% Fe+Cu and few of them between 23 and 28 at.% Fe+Cu (Fig. 6b). Unpublished results of a mineralogical survey of Pt-Fe nuggets, saved from being thrown back to the river in current mining operations on alluvial gold deposits located in the medial reach of the Santiago River too (Yucas, 2017; Lopez-Males, 2017; Castiella, 2018), further confirm the bimodal distribution and the overall Fe+Cu contents of Pt-Fe alloys (the maximum is centered at 16 at.% Fe+Cu) from the Santiago River. This distribution contrasts with that of the Pt-Fe alloys of the historical sample whereby 96.15% of the nuggets contain between 21 and 30 at.% Fe (Fig. 6b). These data suggest that the Pt-Fe nuggets of this historical sample used by Chabaneau to purify platinum did not come from the Santiago River but could have
been collected in a mine located in the proximal or medial reaches of one of the rivers of the Chocó region (Colombia).

The PGM assemblages occurring as inclusions in Pt-Fe nuggets supply additional information to approach the origin of the studied sample. Apart from the presence of osmium, laurite-erlichmanite, bowieite, tulameenite and several minerals of the Pt-Pd-Rh-Ir-Sb-Te system, the most striking feature of this sample is the abundance of Pt-Fe alloys containing emulsion-like inclusions of iridium (~63% of the studied grains). The fact that these type of iridium inclusions were described only in the Nevado and Delfin sampling sites of the Condoto River (Cabri et al., 1996; Weiser, 2002) suggest that this historical sample, very likely came from the proximal or medial reaches of a river in the Chocó region. A reasonable possibility could be the San Juan River, considering the importance of this river in the 18th century for mining operations (Capitán-Vallvey, 1988, 1989) and that many of the mining sites reported in historical documents (Tándó, Opogodó, Itsmina and Novita) are located close to its proximal reach or few kilometers downstream, at the mouth of the Condoto River. PGM inclusions in Pt-Fe alloys further contribute to discard the Santiago river as a source of the historical sample since none of the grains analyzed by Weiser and Schmidt-Thomé (1993) or the 217 grains studied by Yucas (2017), López-Males (2017) and Castiella (2018) contain iridium inclusions. In contrast, the identified assemblages in these inclusions are characterized by abundance of Cu-bearing PGM like honshiiite (PtCu) and cuprorhodsite (CuRh₂S₄) as well as some Pt and Pd sulfides [cooperite (PtS), and braggite (Pt,Pd)S], sperrylite (PtAs₂) and bornite (Cu₅FeS₄) (Weiser and Schmidt-Thomé, 1993; Yucas, 2017; López-Males, 2017; Castiella, 2018).

Mineralogy of platina and the operations for platinum purification

The method of powder metallurgy developed by Chabaneau can be simply summarized in two reactions:
\[
3\text{Pt}_6(s) + 4\text{NO}_3^{-}(aq) + 18\text{Cl}^{-}(aq) + 22\text{H}^+(aq) \rightarrow 3\text{H}_2\text{PtCl}_6(aq) + 4\text{NO}_2(g) + 8\text{H}_2\text{O} \quad \text{(reaction 1)}
\]

\[
\text{PtCl}_6^{2-}(aq) + 2\text{NH}_4^-(aq) \rightarrow (\text{NH}_4)_2\text{PtCl}_6\downarrow \quad \text{(reaction 2)}
\]

By the first one, Pt from platina becomes dissolved in aqua regia as chloroplatinic acid through a complex process that involves chloroplatinous acid \((\text{H}_2\text{PtCl}_4)\) and nitrosoplatinic chloride \((\text{(NO)}_2\text{PtCl}_4)\) and by the second one, Pt precipitates as ammonium chloroplatinate (solubility 0.499 g/100 mL). Alternatively and for reasons of economy, Chabaneau proposed to prepare the aqua regia with nitric acid and common salt with what Pt precipitated as a mixture of alkaline salts \((\text{Na}_2\text{PtCl}_6; 39.7 \text{ g/100 mL}; \text{K}_2\text{PtCl}_6; 1.10 \text{ g/100 mL})\). The thermal decomposition of the salts allowed Chabaneau obtaining malleable platinum by washing with water in case of alkaline salts, hammering the platinum sponge, followed by forging.

However, he often did not achieve satisfactory results since the metal obtained in different runs showed important variations in its characteristics such as the degree of maleability and fragility. According to Chaston (1980), “the ingots, all too often cracked and sometimes even crumbled away under the hammer—all for no apparent reason” and for despair of Chabaneau (Delanoue, 1862). Furthermore, the substitute of Chabaneau in the Casa de la Platina, Joaquin Cabezas, mentioned that problem in a letter sent to the Minister of Finance, Miguel Cayetano Soler in 1804: “I had noticed, a long time ago, that although I always used the same means to purify platina, I did not obtain all bars with equal properties: some possessed all the ductility and softness of this metal, and in others there were a certain rigidity, which did not allow resisting many laminating and drawing operations ” (Cabezas, 1804).

Our results indicate that these effects noticed by Chabaneau were caused by the presence of chemical impurities in platinum, such as other PGE (Os, Ir, Ru, Rh and Pd) since Au, Hg, Pb, Cu and mainly Fe were efficiently removed. Now we know (see Raykhtsaum 2013) that alloying Rh, Ru and, especially Ir with Pt increases the melting point and hardness at reducing malleability, and the addition of Pd to Pt reduces the melting point and slightly...
increases the hardness. This suggests that Chabaneau didn’t controlled completely the platinum purification method, obtaining different platinum metal alloys in different experimental runs. The composition and consequently the chemical properties of the alloys depended on the mineralogical nature of platina and on the parameters of the experimental procedure such as temperature, hydrochloric and nitric acid concentrations, particle size and liquid/solid ratio (Hasani, 2017).

The resistance of the PGE to dissolve from PGM into acids is due to the thermodynamic stability of their crystal lattices as well as the protective effect of the formation of monolayers of metal oxides that passivate the surface. Palladium, platinum and to a lesser extent rhodium and iridium are dissolved in aqua regia via the formation of chloro complexes. The formation of such complexes reduces the standard potential of the system, allowing the oxidation of the metals and promoting their dissolution. In contrast, Os and Ru do not form chloro complexes and their dissolution proceeds by alternate alkaline fusion or better oxidative fusions and subsequent treatment with hydrochloric acid, giving rise to the formation of Os and Ru volatile tetroxides (Tennant, 1804) (Table 4). The values of standard potentials of PGE listed in this table show that Pd and Rh easily dissolve under the redox potential conditions suitable for the dissolution of platinum in aqua regia but Ir requires higher values. Oxidation of Os and Ru even as laurite (RuS₂) to form the volatile tetroxides does not proceed in aqua regia. Thus, dissolution of platina like that studied here via reaction 1 should yield a solution containing Pt, Pd and Rh chloride complexes and an insoluble black residue concentrating Os, Ir and Ru. However, the variability of physical properties of platinum produced by Chabaneau suggests that in some experimental runs Ir could have dissolved, depending on aqua regia concentration, temperature and time conditions, appearing later in the solid platinum. Dissolution of Ir gives rise to a significant change in color in the solution, from yellow (Ir-free) to red (Ir-bearing) (Lewis, 1753). It should be expected that thermal treatment and sintering of (NH₄)₂PtCl₆ containing minor amounts of (NH₄)₂RhCl₆, (NH₄)₂PdCl₄ and mainly (NH₄)₂IrCl₆ give rise to a physical mixture
of Pt, Pd, Rh and Ir. The forging process used by Chabaneau to produce platinum ingots would promote alloying of the small amounts of Pd and Rh detected in platina with Pt but hardly reach temperatures above 1000°C to incorporate Ir in the alloy. Pt-Ir phase relations (ASM Alloy Phase Diagram Database) predicts that below this temperature Pt and Ir remain unmixed and the resulting material turns highly brittle, as Chabaneau very often ascertained.

These experimental problems were approached and solved by Wollaston (1829) by controlling the oxidizing character of the reagent using diluted aqua regia (the method remained secret until he passed away in December 1828). He “recommend, that to every measure of the strongest muriatic acid employed, there be added an equal measure of water”. Dissolution of platina ore with this diluted aqua regia took 3-4 days and required gradual heating. Recent experimental results by Elomaa et al., (2017) support this procedure since they clearly show that both concentration of aqua regia and temperature increase the redox potential of the aqua regia (Fig. 7). As expected from the standard potential values listed in Table 4, this analytical procedure prevented dissolution of Ir, Os and Ru, and consequently left a residuum mainly containing these three metals.

**Provenance of platina and success of platinum purification**

As discussed above, the success of Chabaneau in obtaining purified malleable platinum metal was strongly influenced by the amount of Ir occurring either as inclusions/exsolution lamellae or in solid solution in platina nuggets. Since Ir content in Pt-Fe alloys is similar in all placer deposits studied in the region (Weiser and Schmidt-Thomé, 1993; Cabri et al., 1996; Yucas, 2017; López-Males, 2017; Castiella, 2018), the key factor controlling the quality of platinum metal in Chabaneau's experiments was the presence/absence or mainly the abundance of iridium inclusions in Pt-Fe nuggets. It should be expected that the higher the amount of iridium inclusions in the crude platina was, less malleable and more brittle platinum was obtained. Consequently, any experiment on the sample studied here and on
any other from the same locality (most probably from the Chocó region) should not produce satisfactory results and this might be the reason why Chabaneau rejected such sample and leaved it in the Mineral Museum of the School of Applied Chemistry at El Turco Street.

The presence of a high content of gold in the studied sample (16.61%) does not agree with the fact that the platina shipped to Spain should be the residue left after gold extraction. According to Cabezas (1797) all platina samples he had stored in the Casa de la Platina and in the laboratories of the El Turco street had experienced several treatments to extract gold. Since the methods used at that time to separate gold from platina were amalgamation (by addition of mercury) and inquartation (by addition of silver) (Capitán-Vallvey, 1989) it should be expected some residues or mineralogical evidences of the added metals. During our investigation we didn't observe any traces of mercury or effects of silver addition on gold nuggets; in contrast most gold grains are zoned with almost silver-free rims. These evidences make us suggest that this historical sample is a small portion of the crude material imported to Spain before the establishment of the Platina Monopoly in 1787 and most probably constitute the remaining material of one of the two first shipments sent to Spain in 1767 and 1784 (Table 5). The chemical and mineralogical features of the studied sample, similar to the material exploited nowadays in the Colombian Chocó, suggest a link with the first one, sent from one of the Chocó Royal Boxes (Table 5).

The flow of platina shipments to Spain after the foundation of the Platina Monopoly was carried out through the Royal Boxes of the New Granada Viceroyalty, which were in charge of record taxes for the Spanish Monarchy. Among the 14 Royal Boxes of the Viceroyalty, only those of Santafé de Bogotá (the principal) and the so-called auriferous boxes were related with platina. The latter were those from Antioquia, Popayán, Novita, Citará, Cartagena de Indias and Remedios which in turn had subordinate boxes in charge of separate gold from the crude concentrates extracted from their nearby mines and recover platina to be sent to Spain. According to Table 5, ~69% of the platina shipped to Spain from 1767 to 1805 came from the Chocó area (Citará, Novita and Quibdo Royal Boxes) whereas
only 10.6% came from Popayán. The remaining 20.4% came from Santa Fé de Bogotá and Cartagena de Indias without specification of their local provenance. An exception were the shipments 5 and 6 coming from the Viceroyalty of Peru that were sent by private individuals and not from the Royal Boxes (Capitan-Vallvey, 1999). The random temporal distribution of shipments containing platina from different mining sites might explain the heterogeneous chemical and, mainly mineralogical composition of the crude material used by the lab workers of the Casa de la Platina as well as their bewilderment when obtained different results using the same standard procedure.

Conclusions

The mineralogical study and the historical investigation of a platina sample from the Mineralogical Museum of the School of Applied Chemistry at the El Turco Street, in Madrid, saved from the Napoleonic troops looting in 1808, allow concluding that:

1. This historical platina sample (nowadays at the National Museum of Natural Sciences in Madrid) is a heavy mineral concentrate consisting of Pt-Fe alloy and gold nuggets, associated with ilmenite-hematite, chromian spinel and goethite, as well as with some other minor minerals. Thus, the material known as platina, among other varied names including platina del Pinto, platita, platilla, white gold, and Juan Blanco in the Viceroyalty of New Granada in the 18th century in fact corresponds to Pt-Fe alloy.

2. The Pt-Fe alloy nuggets have a quite homogeneous chemical composition, mainly containing 81.97-90.75 wt.% Pt and 5.08-10.81 wt.% Fe, with minor Cu (0.15-1.1 wt.%), Os (0.07-3.77 wt.%), Ir (<5.62 wt.%), Rh (<2.26 wt.%), Pd (<2.26 wt.%) and Ru (<0.72 wt.%). Their mineralogy is characterized by the presence of a varied set of inclusions of platinum-group minerals: Ir alloys (they occur in 63% of the nuggets),
Os alloys, laurite-erlichmanite, bowieite tulameenite and undetermined Pt-Pd-Ir-Rh antimonides and tellurides.

3. The chemical composition and mineralogical nature of Pt-Fe nuggets are quite similar to those extracted nowadays in the Chocó region (western Colombia), particularly to those from the proximal and medial reaches of the Condoto river, but strongly differ from those occurring in gold placers in the Santiago river in Ecuador.

4. The high Ir content of the studied nuggets seems to be characteristic of the Pt-Fe nuggets mined in the Colombian Chocó and would explain the quite frequent lack of success of the François Chabaneau’s method for purifying platinum. Since he didn’t modify the concentration of aqua regia, he should often have obtained a mixture of \((\text{NH}_4)_2\text{PtCl}_6\) and \((\text{NH}_4)_2\text{IrCl}_6\) which, after forging, gave rise to highly brittle platinum metal due to the presence of unmixed iridium. Only crude platina consisting of Ir-poor, Pt-Fe alloys free of Ir inclusions should have become suitable for obtaining malleable platinum via the Chabaneau’s method.

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FIG. 1. a: Material saved from the Bank of Spain corresponding to the description made by François Chabaneau in his inventory: “two samples of the mineral (platina) and different results of my work with this metal”. The studied sample is the second from the left. b: Mineral concentrate of the studied sample where it is possible to see the Pt-Fe alloy (silver grey) and gold (yellow) nuggets, as well as the ilmenite-hematite (black) grains.
FIG. 2. QEMSCAN digital map showing the mineralogical composition of the studied sample.

The color of each mineral grain corresponds to that used in the lower diagram.
FIG. 3. Statistics of the chemical composition of Pt-Fe alloys in terms of their Fe and Cu contents.
FIG. 4. Representative back-scattered electron images of noble metal mineral inclusions in Pt-Fe alloys. a: irregular gold grains; b: emulsion-like inclusions of Ir alloy, containing significant amounts of Os; c: fine (<0.5 µm) exsolution lamellae of Ir alloy containing significant amounts of Os; d: short tabular lamellae of rather poor Os alloy; e: zoned grain of laurite-erlichmanite; f: several granular inclusions of laurite and bowieite.
FIG. 5. a: zoned gold grain showing a silver-rich core and an irregular, variably-thick rim of almost pure gold; b: gold-bismite intergrowth formed by the decomposition of maldonite (Au₂Bi) into Au and Bi, followed by oxidation of Bi to bismite (note the presence of minute, oxidized inclusions of Bi in gold).
FIG. 6. Comparison of the composition of Pt-Fe alloys of the studied sample with those from different sampling points in the proximal and medial reaches of the Condoto River (Cabri et al., 1996) and from the medial reach of the Santiago River (Weiser and Schmidt-Thomé, 1993; Yucas, 2017, and Castiella, 2018).
FIG. 7. Dependence of redox potential with aqua regia concentration. Inset:

Temperature dependence of redox potential at aqua regia 30%. Modified from Elooma, 2017.
Table 1. Representative electron microprobe analyses of Pt-Fe alloys

|     | 1   | 13  | 16  | 18  | 22  | 23  | 28  | 31  | 40  | 47  | 49  | 55  | 71  | 77  | 86  | 90  | 101 | 102 | 117 | 132 |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| S   | 0.00| 0.05| 0.03| 0.09| 0.10| 0.07| 0.05| 0.06| 0.04| 0.00| 0.08| 0.05| 0.09| 0.06| 0.03| 0.04| 0.03| 0.00| 0.11| 0.04|
| Fe  | 5.08| 7.88| 7.59| 7.36| 9.00| 7.93| 7.91| 10.32|7.85| 8.57| 7.86| 8.23| 7.64| 7.89| 7.72| 8.72| 7.75|10.81|7.59| 8.41|
| Cu  | 0.53| 1.03| 0.97| 0.66| 0.58| 0.74| 0.57| 0.63| 0.56| 0.76| 0.61| 0.51| 0.54| 0.76| 0.67| 0.90| 0.74| 0.56| 1.10| 0.44|
| Os  | 1.53| 0.65| 0.50| 0.40| 0.50| 0.48| 0.29| 0.42| 0.43| 0.39| 0.40| 0.35| 0.49| 0.33| 0.36| 0.49| 0.46| 0.34| 0.59| 0.27|
| Ir  | 0.25| 0.77| 0.88| 2.20| 3.61| 3.14| 0.13| 0.57| 3.36| 1.42| 4.14| 0.37| 5.21| 0.33| 3.08| 0.59| 2.08| 1.11| 0.71| 5.09|
| Ru  | 0.00| 0.00| 0.06| 0.18| 0.64| 0.00| 0.00| 0.09| 0.00| 0.00| 0.30| 0.08| 0.15| 0.00| 0.00| 0.42| 0.00| 0.23| 0.00| 0.09| 0.00|
| Rh  | 1.12| 1.54| 0.44| 0.64| 1.12| 0.39| 0.40| 0.35| 1.10| 1.28| 2.26| 0.26| 1.03| 0.00| 1.06| 1.12| 1.35| 1.16| 0.20| 1.87|
| Pt  | 00.55| 87.43| 88.56| 86.32| 83.33| 85.01| 86.02| 85.76| 85.54| 85.77| 83.06| 80.87| 81.07| 80.74| 85.50| 86.78| 85.16| 84.20| 87.68| 82.18|
| Pd  | 0.50| 0.81| 0.01| 0.84| 0.82| 0.64| 1.46| 1.46| 1.08| 0.87| 0.80| 0.70| 0.75| 1.23| 0.41| 0.70| 2.26| 0.66| 1.07| 0.57| 0.97|
| Total| 0.65| 0.93| 0.04| 0.09| 0.00| 0.10| 0.00| 0.00| 0.00| 0.00| 0.00| 0.22| 0.02| 0.00| 0.02| 0.00| 0.00| 0.00| 0.02| 0.00| 0.02|

|     | Atomic percent |
|-----|----------------|
| S   | 0.00 0.25 0.13 |
| Fe  | 15.44 22.50 22.01 |
| Cu  | 1.40 2.57 2.46 |
| Os  | 1.57 0.54 0.43 |
| Ir  | 0.21 0.64 0.74 |
| Ru  | 0.00 0.00 0.06 |
| Rh  | 1.65 2.06 0.69 |
| Pt  | 78.78 71.02 73.52 |
| Pd  | 0.95 0.57 0.02 |
Table 2. Representative electron microprobe analyses of platinum-group minerals included in Pt-Fe alloys

|       | 4   | 105 | 43  | 66  | 69  | 72  | 108 | 133 | 142 | 91  | 92  | 93  | 158 | 161 | 162 |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| S     | 0.94| 0.00| 0.03| 0.07| 0.04| 0.05| 0.00| 0.00| 0.01| 31.62| 27.95| 28.81| 34.14| 22.88| 27.46|
| Fe    | 0.01| 0.10| 0.35| 1.15| 0.78| 0.35| 1.80| 0.57| 0.71| 0.02| 0.03| 0.05| 0.01| 0.01| 0.00|
| Cu    | 0.00| 0.02| 0.00| 0.01| 0.00| 0.02| 0.00| 0.00| 0.00| 0.00| 0.01| 0.02| 0.03| 0.41| 0.40|
| Os    | 94.98| 93.39| 30.80| 10.94| 19.93| 25.74| 8.00| 24.02| 25.13| 39.49| 50.02| 55.56| 22.45| 0.25| 0.32|
| Ir    | 2.13| 1.20| 53.50| 57.82| 59.88| 59.63| 74.00| 58.06| 60.40| 3.44| 3.41| 3.34| 3.55| 35.53| 34.35|
| Ru    | 0.81| 1.21| 1.85| 1.50| 1.28| 0.53| 1.58| 2.12| 1.12| 22.97| 6.75| 9.66| 36.15| 0.00| 0.00|
| Rh    | 1.73| 2.40| 3.60| 4.05| 4.87| 4.91| 5.63| 5.75| 3.91| 4.24| 3.66| 3.48| 4.10| 37.97| 39.26|
| Pt    | 1.81| 2.79| 11.72| 17.98| 12.89| 9.96| 10.99| 11.32| 9.99| 0.09| 0.29| 0.65| 0.41| 0.96| 0.71|
| Pd    | 0.00| 0.20| 0.50| 0.00| 0.00| 0.18| 0.15| 0.00| 0.00| 0.19| 0.06| 0.00| 0.11| 0.52| 0.00|
| Total | 101.51| 101.29| 102.34| 101.51| 99.66| 101.36| 101.25| 101.84| 101.27| 102.07| 102.17| 101.55| 100.92| 102.52| 102.50|

|       | 4   | 105 | 43  | 66  | 69  | 72  | 108 | 133 | 142 | 91  | 92  | 93  | 158 | 161 | 162 |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| S     | 0.20| 0.00| 0.15| 0.36| 0.21| 0.27| 0.00| 0.00| 0.03| 66.09| 66.13| 66.56| 66.05| 59.02| 59.52|
| Fe    | 0.04| 0.32| 1.10| 3.62| 2.49| 1.12| 5.53| 1.78| 2.27| 0.03| 0.05| 0.07| 0.01| 0.00| 0.00|
| Cu    | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.46| 0.44|
| Os    | 91.48| 89.19| 28.64| 17.49| 18.80| 24.20| 7.12| 21.02| 23.61| 14.17| 24.38| 22.04| 7.46| 0.09| 0.12|
| Ir    | 2.03| 1.13| 49.23| 52.83| 55.89| 55.49| 66.06| 52.68| 56.15| 1.22| 1.37| 1.31| 1.17| 13.26| 12.65|
| Ru    | 1.47| 2.17| 3.24| 2.61| 2.27| 2.94| 2.68| 3.66| 1.98| 15.52| 5.16| 7.21| 22.60| 0.00| 0.00|
| Rh    | 3.08| 4.24| 6.19| 6.91| 8.49| 8.53| 9.39| 9.74| 6.79| 2.81| 2.75| 2.55| 2.52| 26.46| 27.01|
| Pt    | 1.70| 2.60| 10.63| 16.19| 11.95| 9.13| 8.88| 10.12| 9.15| 0.01| 0.11| 0.75| 0.13| 0.35| 0.26|
| Pd    | 0.00| 0.34| 0.03| 0.00| 0.30| 0.15| 0.50| 0.00| 0.00| 0.12| 0.05| 0.00| 0.07| 0.35| 0.00|

Osniom alloys: 4 & 105; Iridium alloys: 43, 66, 69, 72, 108, 133 & 142; Laurite-Erichmanite: 91, 92, 93 & 158; Bowleite: 161 & 162.
Table 3. Representative electron microprobe analyses of gold grains and a gold-bismuth intergrowth

|       | 49-2 | 49-1 | 1   | 2   | 3   | 4   | 15  | 1b  | 2b  | 128b-1 | 128b-2 | 12Au-1 | 12Au-2 | 12Bi-1 |
|-------|------|------|-----|-----|-----|-----|-----|-----|-----|--------|--------|--------|--------|--------|
| Ag    | 16.55| 17.66| 10.34| 5.90| 4.02| 14.05| 7.68| 0.91| 0.29| 0.34   | 1.61   | 0.28   | 0.67   | 0.00   |
| Sn    | 0.10 | 0.07 | 0.11 | 0.00| 0.16| 0.01 | 0.00| 0.15| 0.07| 0.13   | 0.66   | 0.00   | 0.21   | 0.20   |
| Sb    | 0.06 | 0.00 | 0.00 | 0.00| 0.06| 0.00 | 0.00| 0.20| 0.00| 0.00   | 0.00   | 0.13   | 0.07   | 0.14   |
| Fe    | 0.01 | 0.02 | 0.00 | 0.00| 0.03| 0.02 | 0.01| 0.07| 0.08| 0.11   | 0.03   | 0.02   | 0.00   | 0.00   |
| Ta    | 0.00 | 0.00 | 0.00 | 0.00| 0.00| 0.00 | 0.07| 0.00| 0.00| 0.00   | 0.00   | 0.00   | 0.00   | 0.05   |
| Au    | 82.37| 81.04| 89.11| 92.14|94.48| 85.13|90.93|98.61|98.38|98.42   |98.63   |95.78   |95.38   |3.24    |
| Hg    | 0.08 | 0.09 | 0.09 | 0.13| 0.10| 0.02 | 0.00| 0.13| 0.08| 0.14   | 0.11   | 0.12   | 0.18   | 0.00   |
| Bi    | 0.00 | 0.00 | 0.43 | 0.88| 0.00| 0.32 | 0.30| 0.00| 0.34| 0.00   | 0.46   | 3.06   | 0.00   | 94.43  |
| Total | 99.18| 98.89| 100.64|99.15|98.78| 96.54|99.43|100.07|99.73|99.14   |100.50  |99.38   |99.90   |98.06   |

Atomic per cent

|       | Ag  | Sn  | Sb  | Fe  | Ta  | Au  | Hg  | Bi  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|
| Ag    | 26.7 | 0.15 | 0.08 | 0.04 | 0.00 | 72.9 | 0.08 | 0.00 |
| Sn    | 0.11 | 0.00 | 0.00 | 0.00 | 0.00 | 71.3 | 0.08 | 0.00 |
| Sb    | 0.17 | 0.00 | 0.00 | 0.00 | 0.00 | 81.6 | 0.14 | 0.00 |
| Fe    | 0.61 | 0.00 | 0.00 | 0.00 | 0.00 | 83.5 | 0.12 | 0.00 |
| Ta    | 0.26 | 0.00 | 0.00 | 0.00 | 0.00 | 25.0 | 0.00 | 0.00 |
| Au    | 13.0 | 0.00 | 0.00 | 0.00 | 0.00 | 37.6 | 0.10 | 0.00 |
| Hg    | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 |
| Bi    | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

Au (core): 49-1, 49-2, 1, 2, 3, 4 & 15; Au (rim): 1b, 2b, 128b-1 & 128b-2; Maldonita (Au): 12Au-1 & 12Au-2; Maldonita (Bi): 12Bi-1
| Oxidized form | Reduced form | $E \text{ V}$ | Reference |
|--------------|--------------|---------------|-----------|
| O$_2$        | Os           | 0.838        | Lide (2003) |
| IrCl$_6^{2-}$| Ir           | 0.835        | Harris (2010) |
| PtCl$_6^{4-}$| Pt           | 0.755        | Lide (2003) |
| PtCl$_6^{3-}$| Pt           | 0.744        | Kanamura & Yagyu (2016) |
| PdCl$_4^{2-}$| Pd           | 0.646        | Polotnyenko & Khodakovskii (2014) |
| RhCl$_6^{3-}$| Rh           | 0.431        | Lide (2003) |
| Shipment | Year of arrival | Weight, kg | Origin (Royal Box)                  |
|---------|----------------|-----------|------------------------------------|
| 1       | 1767           | 21.82     | Chocó                              |
| 2       | 1784           | 59.51     | Santafé de Bogotá                 |
| 3       | 1787           | 19.32     | Santafé de Bogotá                 |
| 4       | 1787           | 70.94     | Popayán                           |
| 5       | 1787           | 32.14     | Lima                              |
| 6       | 1787           | 194.58    | Lima                              |
| 7       | 1789           | 1310.16   | Citará/Nueva                       |
| 8       | 1790           | 20.9      | Cartagena de Indias               |
| 9       | 1791           | 520.26    | Citará/Nueva                      |
| 10      | 1791           | 4.42      | Popayán                           |
| 11      | 1791           | 46.4      | Citará/Nueva                      |
| 12      | 1795           | 67.3      | Quibdo/Nueva                      |
| 13      | 1802           | 10.43     | Santafé de Bogotá                 |
| 14      | 1802           | 44.04     | Santafé de Bogotá                 |
| 15      | 1802           | 227.04    | Santafé de Bogotá/Popayán         |
| 16      | 1803           | 10.12     | Cartagena de Indias               |
| 17      | 1804           | 134.54    | Santafé de Bogotá                 |
| 18      | 1805           | 52.77     | —                                  |