Early Studies of Platinum in Spain

THE CONTRIBUTION MADE BY JOSEPH LOUIS PROUST

By R. Moreno García

Unidad Docente de Química, E.T.S.I. de Montes, Universidad Politécnica de Madrid, Spain

A critical study is presented here of the contribution made by Joseph Louis Proust, Professor of Chemistry and Metallurgy at the Royal Artillery School in Segovia, to the early investigation of platinum. His researches were carried out in Spain, mainly at the Segovian House of Chemistry during the latter years of the eighteenth century, and at the platinum laboratory in Madrid in the early years of the nineteenth century. These investigations resulted in three papers about the metal; one of them is almost unknown, but it gives a procedure which he had established for the possible purification of platinum. In the other two, Proust incorrectly interpreted the results of his experimental work, but he showed a systematic approach to his scientific investigations and paid great attention to detail, being the only investigator of platinum in Spain at that time to do so.

Following the formal announcement of the discovery of platinum by A. Ulloa in 1748 (1), there was great interest throughout Europe in the investigation of this substance. In 1752 the Swedish scientist Henrik Theophil Scheffer, in 1754 the Englishman William Lewis, in 1757 the German chemist Andreas Segismund Marggraf, and the following year the Frenchmen Pierre Joseph Macquer and Antoine Baumé, provided the first important chemical/metallurgical

Joseph Louis Proust
1754–1826

Born in Angers, France, Proust spent three years at Vergara in the Seminario Patriótico. In 1788, he was appointed Professor of Chemistry and Metallurgy at the Royal Artillery School at Segovia, by the King of Spain. In the laboratory in Segovia, which was reputed to be equipped with platinum apparatus, and later on in Madrid he established a working procedure for the purification of platinum. His laboratory in Madrid was destroyed in 1808 during the siege of Madrid by Napoleonic forces

contributions to the systematic study of platinum, this new metal from South America (2).

Spain could not stand aside from the investigation of this "Exclusive Spanish Metal", as it was referred to by Herrgen (3). However, the scientific facilities available in Spain at that time, especially in the field of chemistry, were hardly adequate for the adulteration of gold with platinum to be investigated in an effective way. This fraudulent use of platinum was practised habitually in Spanish America (4), with unfortunate economic consequences for the Spanish Crown. None the less the botanists Cristobal Vélez and Pehr Löfling, and the Irish naturalist William Bowles (1705–1780) investigated platinum in the early 1750s, although their investigations were not necessarily directly related to the problem of gold adulteration. Indeed, we think that they were probably carried out solely for scientific interest (5).

During the latter part of the eighteenth century, however, investigators in Spain achieved some success. In 1786, a young Frenchman named Pierre François Chavaneau (the Spanish spelling is Chabano) and his Spanish silversmith Francisco Alonso became the first people in metropolitan Spain to achieve purification of native platinum, so facilitating its industrial application and enabling smiths to manufacture platinum articles of fine quality. This epoch was named by Don Juan Fagés y Virgili as the "Platinum Age in Spain" (6), a most fortunate expression that has been revived in the definitive work on the history of platinum (7).

The contribution by Louis Proust was made at the end of the "Platinum Age in Spain", that is in the last years of the 18th century and the early years of the 19th century. Three publications about platinum resulted: the first of these was published in 1795 in volume two of the *Anales del Real Laboratorio de Química de Segovia* (8), the second appeared in the *Anales de Historia Natural de Madrid* in 1799 (9) and, finally, a letter sent to Nicholas Louis Vauquelin (1763–1829) on 6th November 1803 was published in Paris in the *Annales de Chimie* the following year (10).

In the prologue to the first of these three communications, Proust had noted "To the Memories that compound this notebook we could add a lot more about the animal analysis, about the platinum". Clearly by that time Proust must have been knowledgeable about platinum, most likely because he had carried out investigations in Segovia during the early 1790s. Later, of course, he would have performed experiments in Madrid at the Turco Street laboratory where he was in charge during 1799, following the departure of Chavaneau in 1797 (11). Some of Proust's observations were probably contained in the letter that he sent to Vauquelin, as certain manuscripts and documents relating to Proust are known to exist in the Indian Archive of Seville.

For the present, we shall ignore whether Proust was ordered to investigate platinum, or if the research was done by "motu proprio" (his own wish). However, on 27th April 1786 his great protector, the Count of Lacy requested the Marquis of Sonora to make some platinum available to Louis Proust, who the King of Spain had just appointed Professor of Chemistry and Metallurgy at the Royal Artillery School at Segovia.This was to enable Proust to increase his knowledge of platinum which he could then communicate to his students, as well as to assess the advantages that could be gained from the use of this metal (12).

The First of the Publications

The brief note that he published in the "Anales de Química de Segovia" can be translated as follows:

> "Platinum. All the ones that I have examined contain copper. If a solution of platinum is precipitated by a plate of pure iron, and the nitric acid is applied to the precipitated platinum, the copper and the oxide of iron are taken out; and pouring hepatic water in this acid copper is precipitated".

Thus he gives a practical and efficient method of eliminating the copper contained in the platinum by the use of "hepatic water", an aqueous solution of hydrogen sulphide.He describes the procedure succinctly, but he does not give it as a method for refining platinum. The reported procedure, however, would have resulted in a substantial purification of the native platinum and it is possible that Proust would have used this

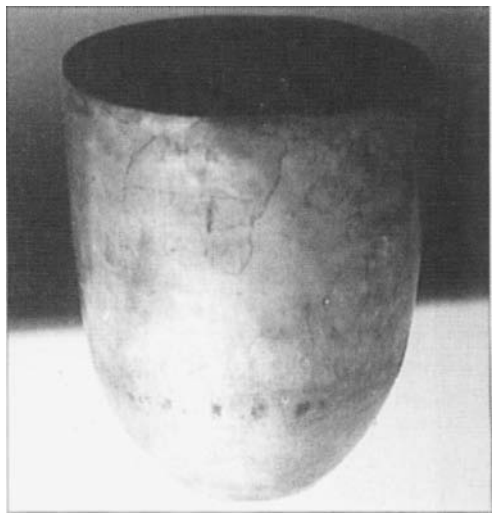
Native Platinum Ore		
	Chocó	Pinto river
Element	Composition, per cent	
Pt	86.16	84.34
Pd	0.35	1.66
Rh	2.16	3.13
Ir	1.09	2.58
Os	0.97	0.19
Ru	0.00	0.00
Fe	8.03	7.52
Cu	0.40	traces
Mn	0.10	0.31
Os-Ir	1.91	1.56

method to purify the inferior platinum sent to him from Chavaneau's laboratory in Madrid. This view is supported by a communication from the Segovia laboratory dated 1791, in which he asks for unpurified platinum to be sent to him so that he could use it for fabricating crucibles (13). This suggests that he had at his disposal a more adequate refining procedure than the one used by Chavaneau.

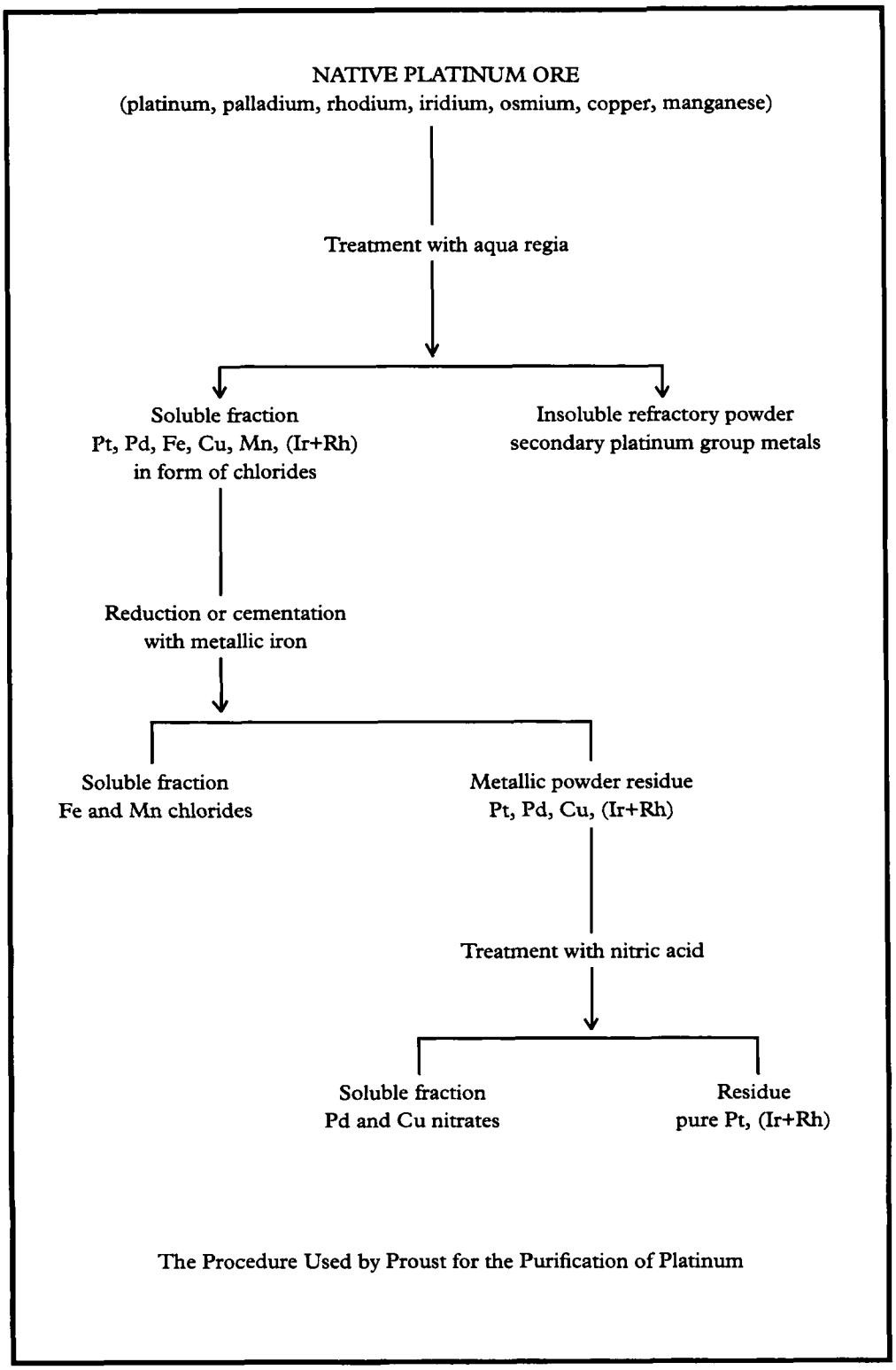
The procedure he describes consists of treating the solution of platinum in aqua regia by the cementation of the metals dissolved in it with an iron plate; the metallic powder obtained in this reduction was later treated with nitric acid, and the copper in this solution was detected with hepatic water.

The general composition of the native platinum from the Choco and the Pinto River, as given by Svanberg (14), is shown in the Table.

Treatment in aqua regia will dissolve all the platinum and palladium, as well as iron, copper and manganese; but because the rest of the platinum group metals are practically insoluble in aqua regia a very refractory powder remains. By repeated attacks with this solvent, and with considerable difficulty, a partial dissolution can be achieved. Treatment of the platinum solution in aqua regia with an iron plate, as indicated by Proust, would give a precipitate in powder form, made up of a mixture of platinum, palladium and copper. The iron and the manganese would not be reduced by the metallic iron but would stay in the solution. Treatment of the powder mixture with nitric acid would dissolve the copper and the palladium as nitrates, while leaving the platinum powder in a practically pure form. Thus the procedure offered a worthwhile route for the elimination of iron, which was abundant in the platina ore. The elimination of iron constituted a major advance in the production of



A platinum crucible conserved in the Artillery School of Segovia, the construction and use of which is attributed to Louis Proust, although no documentary evidence for this exists. The height of the crucible is approximately 8cm



The Procedure Used by Proust for the Purification of Platinum

platinum metal; Chavaneau's method of precipitation with potassium chloride or ammonia, as well as the techniques used by other investigators, resulted in the retention of a certain amount of iron which later decreased the malleability of the platinum. The procedure that we assume Proust used for the purification of platinum is shown here schematically.

This procedure has been, and indeed still is, very important in noble metals refining where the cementation of the platinum group metals by zinc or iron powders is employed at different stages in the separation.

The Second Publication

The second of Proust's publications about platinum was a lengthy article divided into fifteen chapters which appeared in the *Anales de Historia Natural* in 1799. The more important aspects of this article, which is perhaps the least analysed of Proust's work, are now considered:

In Chapter III he writes about the presence of gold in the platinum, evaluating the former at about 10 per cent and noting that he had already communicated this figure to the Ministry. This tends to confirm the inadequacy of the amalgamation method of separation, as carried out in Spanish America during the eighteenth century and which continued until the end of the colonial period.

In Chapter IV Proust makes one of his more important mistakes when he assumes that the platinum occurs as a sulphide and therefore is bound to sulphur. He makes this major error because of his incorrect interpretation of the platinum calcination experiments, and in doing so he lost an opportunity to identify a new element.

By means of a blowtorch he heated the platinum on a coal support, reporting that "it exhales a penetrating steam of sulphur accompanied by smoke" and that when he made the experiment in a closed crucible this did not happen, but as the crucible was uncovered "you can detect this smell stronger". Later on, he continues "I have not been able to know the character of this steam for a long time, but at the end of these experiments it would seem that what I have found is nothing other than concentrated sulphuric acid".

When he obtained this penetrating steam of unknown character, Proust probably associated it with sulphur, but in fact the native platinum ore does not contain sulphur, neither does it appear to be accompanied by any sulphur-containing minerals. In all probability, therefore, the so-called "steam" was osmium tetroxide. Thus, we might say that Proust let an opportunity to discover osmium "evaporate into thin air".

Another error occurs in Chapters VI and VII, which relate to the insoluble residue of the platinum solution in aqua regia. He observes that the residue can vary from 1.5 to 3.5 per cent depending on the type of sample and, incomprehensibly, he believes it to be graphite. This is an inexplicable association because in the text he reports that "in the course of the platinum dissolution it seems to be reduced to a black powder, not less heavier than the platinum". If it was the same density as platinum, it is difficult to understand why he associated it with graphite, the density of which at 2.25 g/cm^3 is less than one-ninth that of platinum. This error deprived him of a chance to discover the existence of another new metal, namely iridium. As with osmium, Proust let the opportunity "slip through his fingers". He continued with this error until at least 1803 when in his letter to Vauquelin he again alludes to the insoluble residue as graphite; in fact it was Vauquelin who recorded in a footnote that the material which Proust referred to as graphite was a new metal.

In Chapter IX and later, Proust describes the dissolution of platina in aqua regia and records that the platinum dissolutions in this solvent, when taken to total dryness, are only partially insoluble and that the portion which does not dissolve is a little known acid, "muriato" (chloride). This was probably caused by the formation of insoluble rhodium trichloride, but once again Proust did not consider the possibility of other metals being present in the native platinum, and therefore he did not investigate the fact that one portion of the precipitate was soluble while the other was insoluble. He observed that solutions of black platina were redder than those of white platina, but did not attempt to explain this. In fact, the black platina contains a

greater amount of palladium and rhodium; when dissolved, these metals give a strong red coloration.

Finally, he observed that the precipitation of insoluble potassium chloroplatinate in the platinum solutions in aqua regia, was due to "saltpetre" (potassium nitrate), which exists as a contaminant in commercial nitric acid and was present in the collar of the retorts.

Proust did not refer to the possibility of using chloroplatinic acid as a selective reagent to distinguish between sodium and potassium salts, as only the latter precipitate. However, the author of the preceding article in the 1799 issue of *Anales de História Natural* (15) acknowledged that it was Proust who proposed that the reagent of the platinum dissolutions could be used to distinguish between the sodium and the potassium salts.

The Letter to Vauquelin

In the third of his publications about platinum, in which he continued to refer to the insoluble residue as graphite, Proust made two important proposals:

First, that a mixture of nitric acid and marine salt could be used instead of aqua regia to dissolve platinum, giving a platinum chloride "barrillé" (sodium), and he commented that its crystallisation was very easy and useful for the separation of iron chloride. Although not the first time that this mixture had been proposed as a solvent for platinum, the comment was very pertinent as the sodium platinum group metal salts formed would be easily crystallised and very soluble. In these circumstances, the rhodium forms a soluble sodium chlororhodite, and he would not find the insoluble fraction which appeared when he took the platinum dissolution in aqua regia to dryness.

His second proposal for the precipitation of platinum concerned the use of soluble sulphides instead of ammonium chloride

> "as the black precipitates that are formed with the platinum lose the sulphur very easily and give a pure platinum powder that it can be agglutinated and forged, as with the ammonium salt".

Again Vauquelin made a very pertinent comment: that the procedure would not be appropriate because it did not take account of the new metal, by which he meant palladium; even though Proust knew of the recent publication which reported the existence of palladium, apparently he had not considered the possibility of separating the two metals.

Acknowledgements

This paper is based, in part, upon a presentation made to the International Congress on Louis Proust, held in 1992 to commemorate the bicentenary of the inauguration of the Segovian House of Chemistry. My thanks are due to Professor R. Fernández de Caleya and L. Fernández Pacios who read this manuscript and made useful suggestions.

References

1 A. Ulloa and J. Juan, "Relación Histórica del Viaje a la América Meridional", Madrid, 1748, A. Marín, **2**, (I), p.606

2 See for example D. McDonald, "A History of Platinum", Johnson Matthey, London, 1962; D. McDonald and L. B. Hunt, "A History of Platinum and its Allied Metals", Johnson Matthey, London, 1982

3 E. Maffei, "Centenario de la Escuela de Minas de España, 1777–1877", ETSI de Minas, Madrid, 1977, p.14

4 A. Galán and R. Moreno, *Platinum Metals Rev.*, 1992, **36**, (1), 40

5 A report of the investigations undertaken by the three named scientists has been prepared for publication elsewhere

6 J. Fagés Virgili, "Los Químicos de Vergara y sus Obras", 1909, maiden speech at *Real Academia de Ciencias Exactas, Físicas y Naturales*, p.59

7 D. McDonald and L. B. Hunt, "A History of Platinum and its Allied Metals", Johnson Matthey, London, 1982, p.93

8 L. Proust, *Anal. Real Lab. Quím. de Segovia*, 1795, **II**, 114

9 L. Proust, *Anal História Natural*, 1799, **1**, 51

10 L. Proust, *Annal. de Chim.*, 1804, **49**, 177

11 Archivo de Indias, Leg.835, 1797, pp.323–362

12 *Ibid.*, pp.141–186, doc.5j

13 Quoted by L. Silvan, *Boletín Real Soc. Bascongada de Amigos del Paris*, 1969, S. Sebastian, Año XXV, 1er cuaderno, p.183

14 F. Stohmann and B. Kerl, "Gran Enciclopedia de Química Industrial", Barcelona, 1930, Francisco Seix, Tomo **XI**, p.457

15 D. Garcia Fernández, *Anal. Historia Natural*, 1799, **1**, pp.46–51