Platinum in the Eighteenth Century

A FURTHER SPANISH CONTRIBUTION TO AN UNDERSTANDING OF ITS DISCOVERY AND EARLY METALLURGY

By A. Galán and R. Moreno

Department of Chemistry, Informatic Faculty and E.T.S.I. de Montes, Polytechnic University of Madrid, Spain

It is generally accepted that the first description of "platina" to appear in Europe was by a young Spanish naval officer, Antonio de Ulloa, whose famous work "Relación del Viaje a la América Meridional" was published in 1748. Important though this was, of even greater significance was the fact that the primary metallurgy of platinum must have been established much earlier, enabling it to be extracted, purified and manufactured. These processes appear to have been kept secret from other European countries, and until recently their details had not been deduced. Now manuscripts discovered in the Colombian Archives enable known methods of purification to be linked to the description of the primitive manufacturing process.

The date of the discovery of platinum has often been debated, but current opinion favours the claim of Antonio de Ulloa (1) over that of Charles Wood (see (2) where W. Watson refers to a letter in which C. Wood communicated to him in 1741 the existence of platina). Earlier this century, however, in a little known publication, a Peruvian historian named Luis Ulloa ascribed the discovery to José Sánchez, a Spanish assayer who had worked at the Casa de la Moneda de Santa Fé de Bogotá (3). Unfortunately Luis Ulloa did not support this attribution with any bibliographical evidence. From his biographical details, however, there is no doubt that he was extremely knowledgeable about the archives of Colombia, Ecuador and Peru, and therefore it would not be surprising if he knew of the existence of documents concerning platinum that pre-dated the arrival in South America of Antonio de Ulloa.

In a work published in 1985 (4) Espinosa Baquero, a Spanish-American author, reproduced a manuscript by José Sánchez de la Torre y Armas (5). This included a balance sheet, dated 1726, for a separation of gold and platinum, and is very likely the manuscript referred to earlier by Luis Ulloa, when attributing the discovery of platinum to Sánchez.

The Sánchez manuscript has been studied by Espinosa Baquero and also by Luis Fermín Capitán (6) but their interpretations of the separation procedure differ from that of the present authors.

Background to the Early Metallurgy of Platinum

Historically the significance of the various claims concerning the discovery of platinum, arising from the writings of Ulloa, Wood and even Sánchez, have been complicated by the fact that they considered only the native metal, "platina", which may have been adulterated with other metals, and which received no kind of scientific purification.

Of even greater importance is the fact that fabricated platinum articles existed in the first third of the Eighteenth Century, necessitating a refining or purification process and, in the absence of the means to melt it, a hot-pressing or sintering process that enabled the platinum to be worked subsequently (7).

The possibilities of platinum fabrication were

acknowledged by experts in other European countries, dating it before the voyage of Antonio de Ulloa to South America. In a letter from William Watson to Georg Mattias Bose, dated 15th January 1751, (included in the review by M. Morin (8)), the following reference is made to "platina":

> "It is not possible to forge, but it has already been found in America the way of moulding hilts of swords".

On the other hand, in 1750 Watson had already noted in the *Philosophical Transactions*:

> "But the Spaniards have a way of melting it down, either alone, or by means of some Flux; and cast it into Sword-hilts, Buckles, Snuff-boxes, and other Utensils." (2)

Charles Wood adds (see (8) pp.31–32) that they may achieve the fusion by adding another metal, or non-metal. He supports this assertion by referring to cupellation experiments carried out in Jamaica by M. Brownrigg, where a weight loss occurred during the process due to impurities. However, cupellation was not a guarantee of pure platinum, as it would not be possible to eliminate all the lead from the cupellation residue because of the solidification of the lead-platinum alloy prill before the cupellation was properly finished. None the less, objects made from pure platinum may have existed, and if they did then they could have been taken from Cartagena de Indias to Jamaica where Wood could have obtained them.

In his survey of the literature on platinum, Morin writes—although possibly without first hand knowledge:

> "The Spaniards have found the secret of its fusion, since they have fused hilts of swords, boxes, tobacco-boxes, etc...." (8)

These comments were all corroborated in a much later, 1774, report on platinum by José Celestino Mutis, Director of the Real Expedición Botánica al Nuevo Reino de Granada, the manuscript being in the Real Jardín Botánico de Madrid (9). Referring to earlier times, Mutis notes that:

> "Although in this city, small pieces of platina were fused years ago, forming hilts for ceremonial swords, boxes and buckles, not any piece is to be found today, either for the no appreciation that this invention got from its residents, or for the requests from foreigners who wanted to verify the fact of the fusion they doubted about, they have entirely vanished".

This is not a technical report, but it gives the opinions of Mutis upon the advantages of platinum for industrial applications. It includes a report of melting tests carried out in the Casa de la Moneda de Santa Fé to make two medals embellished with the head and shoulders of the King.* Although no details of the refining or melting procedures are given, Mutis says:

> "The fusions that on this occasion have been practiced in order to form those samples, have been very easy and yet without all that difficulty . . . with the result that, being the fusion of this metal very easy . . .
> The portrait of the royal person in medal number 1 is the sample of the pure platina . . ."

Thus, it seems unquestionable that pure platinum could be "melted", although this may actually mean "hot-forged", but the result for medal number 1 was not excellent. The craftsman who carried out the "melting" was Francisco de Benito, the engraver at the Casa de la Moneda de Santa Fé. According to Manjarrés (10), the Junta de Comercio asked for information about the method used by Benito, the engraver from la Ceca, who had been awarded a prize for discovering the procedure which he had been recommended to keep secret. This he apparently did, because there is no record of it in the Archivo General de Indias.

The medals resulted from a revival of interest in platinum by the Junta de Comercio, who knew of the Santa Fé directive concerning platinum. According to Manjarrés, this directive required that the platinum which was separated from gold in the Casas de la Moneda was to be thrown into the rivers, as it was impossible to melt, but more especially to avoid its fraudulent use as an adulterant. The Viceroy

*In Reference 10, Manjarrés indicates that the American publisher José Toribio Medina possessed a platinum medal from Santa Fé which carried a bust of King Carlos III, and wonders if this medal was one sent by the Viceroy.

encouraged experimentation with the platinum, and in 1774 he reported that although it had not been known how to melt platinum, this had now been achieved as a result of the experiments carried out; as proof of this he sent the medals carrying the portrait of the King, as related by Mutis.

With hindsight it seems curious that a melting process was not known in Santa Fé, although one had been available earlier. It is, perhaps, also surprising how quickly it was rediscovered when experimentation started. Again, it is interesting to consider that before the arrival of Ulloa platinum had been fabricated in a primitive way, but over a period of only thirty years this ability had been lost, perhaps due to lack of interest.

Thus, as a working hypothesis we will assume that Francisco de Benito re-discovered the process that had been used in la Ceca in the first part of the century, making use of information contained in a manuscript stored in the Casa de la Moneda de Santa Fé which he was probably able to access when commencing his study of the fusion of platinum.

The Bogotá Manuscript

The manuscript of José Sánchez de la Torre y Armas contains a mass balance and a cost analysis for refining a batch of gold which contained platinum (5). The report is unclear because it mixes the language of the time, which was probably associated with commercial aspects of the process, with mention of the balances. The author makes no attempt to describe the technical aspects of the process used; this has to be deduced from the comments that he makes about the difficulties of the process as he tries to justify the high costs involved. Important technical conclusions about costs and weights of materials can be deduced from the report, as will now be demonstrated.

The Separation Procedure

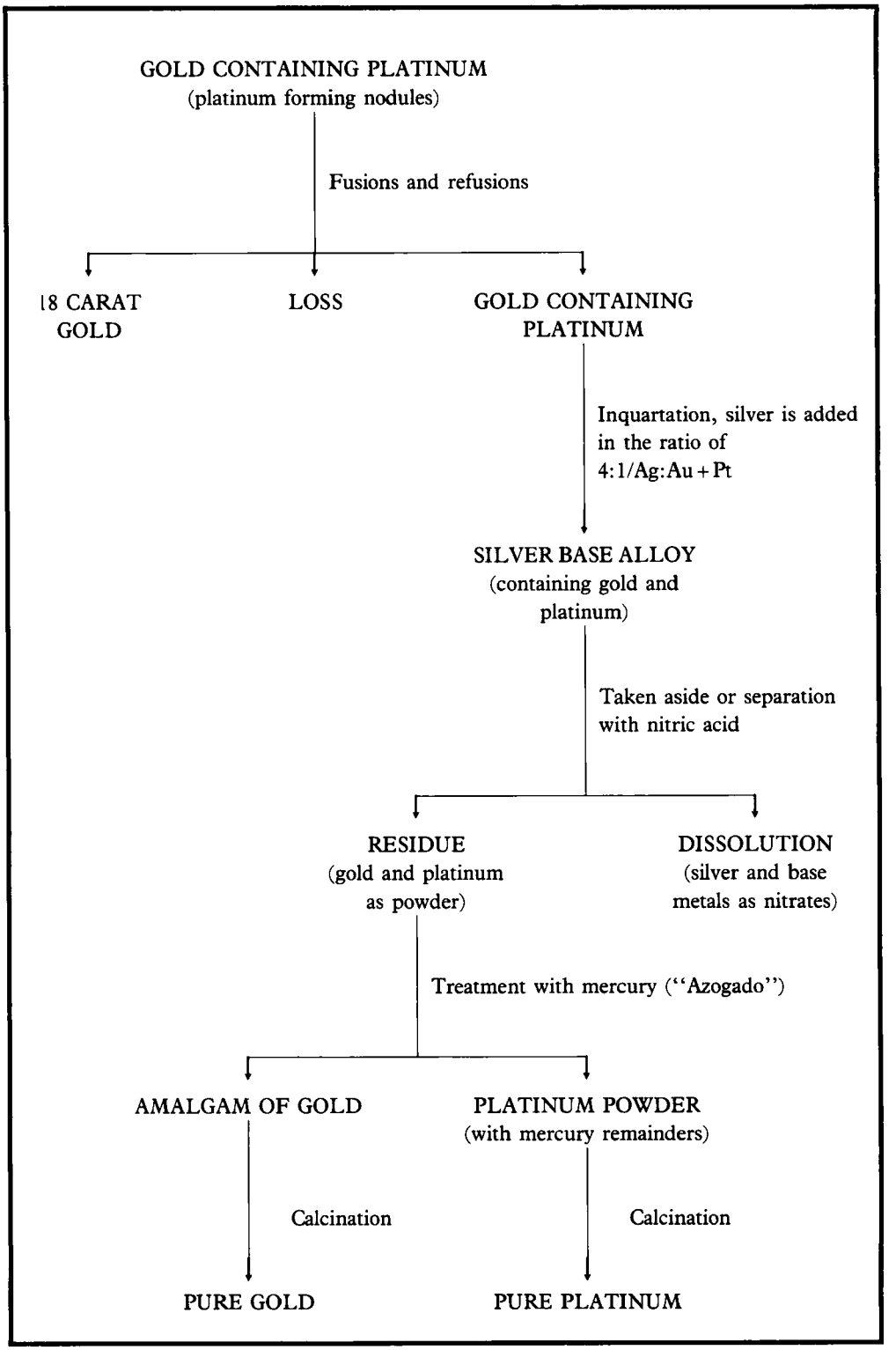
The manuscript refers to six bars of gold mixed with platinum and having a total weight of 5958 castellanos. The origin of the bars is not given and, therefore, it is not known whether they consisted of primary un-refined gold which naturally contained platinum or were gold adulterated with platinum.

By virtue of the first refining procedure adopted, we are of the opinion that the bars were new un-refined material. Initially the gold was melted several times to give what Sánchez regarded as "clean" 18 carat gold, free of platinum, together with a gold residue which contained the platinum. There was, additionally, a melting loss of 58 castellanos. Clearly the gold and platinum cannot have been perfectly alloyed, since if they had been they would have been inseparable by simple melting. It must be concluded that the platinum was present as particles in the body of the gold, resulting from incomplete initial fusion before the bars were cast. When the gold was re-melted, the insoluble platinum could be separated with a strainer.

This procedure saved Sánchez from having to refine the whole of the 5958 castellanos by the next procedure, known as inquartation.

A flow-sheet of the whole process is shown in the Scheme. In the manuscript Sánchez claims that he obtained 3000 castellanos of clean gold, free from platinum, although admittedly only 18 carat. This is unlikely to be strictly true since some platinum would probably have dissolved during the melting processes, although possibly only trace amounts. This does not seem to have been noticed by him, and it would not have changed in a perceptible way the colour or the melting point of the gold, or its mechanical properties. Also, at low concentrations it would have been difficult to detect by fire assay.

It is considered that both the separation by melting and the formation of an 18 carat alloy are evidence that the bars had originated from the incorrect melting of natural gold, containing some platinum. If the gold had been intentionally adulterated, the separation would be impossible if alloying had occurred, and the gold alloy would probably have been of a higher quality, for example, a 22 carat coinage alloy. Also in an adulterated alloy the platinum would presumably have been well alloyed in order to make it more difficult to detect.


GOLD CONTAINING PLATINUM
(platinum forming nodules)
Fusions and refusions
18 CARAT GOLD
LOSS
GOLD CONTAINING PLATINUM
Inquartation, silver is added in the ratio of 4:1/Ag:Au + Pt
SILVER BASE ALLOY
(containing gold and platinum)
Taken aside or separation with nitric acid
RESIDUE
(gold and platinum as powder)
DISSOLUTION
(silver and base metals as nitrates)
Treatment with mercury ("Azogado")
AMALGAM OF GOLD
PLATINUM POWDER
(with mercury remainders)
Calcination
Calcination
PURE GOLD
PURE PLATINUM

The second part of the procedure for refining the gold is based on inquartation, which is a well known process for refining gold although little used in practice. It is based on the solubility in nitric acid of silver and the base metals commonly present in the alloy. The gold to be refined is melted with three to four times its weight of silver; when this alloy is treated with nitric acid everything dissolves except the gold which remains as a powder at the bottom of the container, and can be easily separated by decanting the solution. This method is unlikely to have been used for normal gold refining because of the high cost of nitric acid, as will be shown later in the analysis of costs. Other methods such as "real foundation" and "fusing precipitation" (12) might have been preferred, the use of inquartation being limited to assaying. But it will be shown next that inquartation was the only process available to Sánchez which could have been used to separate platinum and gold.

Sánchez carried out the inquartation correctly, using a 4:1 ratio of silver to the 2900 castellanos of platinum-containing gold, in order to transform the gold-base metal alloy into a silver-base metal alloy soluble in nitric acid. The problem he faced, as he acknowledged, was in achieving an homogeneous alloy since the platinum did not alloy readily with silver at the temperature of his furnaces. He notes:

> ". . . happening to make a new alloy in some granules, when the platina flocculates and does not have itself enough silver, for the water to cause its effect".

It was necessary for the alloy to be homogeneous, so that when the silver dissolves it leaves behind a finely divided residue of gold and platinum and not platinum nodules. Actually, under these conditions platinum has some solubility in nitric acid, particularly in strong acid (but this would not necessarily have been available in this case), something which does not happen with gold. However, we do not think that this solubility is likely to have been noticed by Sánchez.

Thus, after the inquartation a mixture of gold and platinum powders is left; the silver and base metals having been dissolved in the nitric acid. Sánchez does not specifically indicate how he achieves the further separation of the two noble metals, but the key information is contained in the detail of the costs:

> "Por el costo que hay y que se tuvo . . . plata consumida, peones, azogado del oro que sale para separar la platina calcinada . . ."
> ["By the cost that there is and was . . . consumed silver, labourers, treatment with mercury of the leaving gold in order to separate the calcined platina . . ."]

There seems to be little doubt that he separated the platinum and gold by amalgamation with mercury, which would rapidly dissolve the fine gold powder leaving behind the platinum which does not alloy with mercury. This residue would then be calcined to yield practically pure platinum.

Espinosa Baquero, in his interpretation of the process, suggested that aqua regia was used rather than nitric acid (4), basing it on a remark by Sánchez "that it dissolves the gold and the platinum". Sánchez does not mention aqua regia, however, and the large mass of silver based alloy would be unlikely to dissolve in the reagent owing to the formation of insoluble silver chloride; this would prevent or make difficult the dissolution of the rest of the alloy.

Capitán proposes that the platinum is all dissolved by the nitric acid (6), this assumption possibly being based upon the work of Mathieu Tillet (1714–1791). This work was not published until 1779, however, so the information would not have been available to Sánchez in 1726; even if they had been contemporaries they were unlikely to have meet in Santa Fé. Furthermore, the solubility of platinum in nitric acid is quite limited and repeated cupellations and partings in nitric acid would be required to effect a separation.

Having obtained a solution of platinum in nitric acid, Capitán next proposes that Sánchez separated the silver from the platinum by cementation with brass, but this process was not widely known at that time.

The procedure that we deduce from the manuscript is in keeping with the information known at that time; in addition to the fact that

it was mentioned in the Sánchez manuscript, the amalgamation process was well known at that time, being used on alluvial gold grains to separate them from admixed platinum particles.

We have deduced from the manuscript that Sánchez was neither a scientist nor an investigator. He is far more likely to have been an assayer applying the established procedures of his craft. It is probable that these assay procedures had been known in the Ceca de Santa Fé for some years and were passed from one assayer to another, as was the case with other craftsmen's knowledge at that time. For the moment, however, this is the oldest written document on the subject from which any technical conclusions can be drawn.

In the light of present knowledge, we consider that the platinum obtained by Sánchez would have been practically pure, although it is certain that his objective would have been the separation of platinum from the gold, rather than the refining of the platinum. Sánchez states that he produced calcined platinum and platinum grains, in which state the platinum could be readily hot-forged. This suggests an improvement in the mechanical properties compared to those of native platinum, which was not malleable and could not be worked.

Since the process described was the only one then available for the production of pure platinum, we propose that it may well have been the one used for the platinum that was fabricated into the buckles, boxes and other articles which circulated in the neighbourhood of Santa Fé de Bogotá.

It also seems likely to have been the process used many years later by the engraver Francisco de Benito to mint the medals that carried the King's bust.

Finally, it is surprising that the gold separated by the nitric acid and amalgamation stages should have the unusual fineness of 21 carat. Gold refined by this procedure would normally be expected to be almost pure.

The Analysis of Costs

The study of the refining costs presented by Sánchez is very interesting because of the picture it presents of the problems, both technical and economic, that were caused by the adulteration of gold with platinum.

Table I

Yields and Costs of the First Refining

Gold obtained = 2250 castellanos of fine gold (3000 Cs 18 carat gold)
Value of this gold = 6474·4 patacones
Cost of the loss in gold = 105·14 patacones (58 Cs of original alloy*)
Fusion cost = 323·66 patacones**

Total cost = 428·8 patacones

* We suppose the original alloy to be of an average fineness of 630 0/00 in gold.
** He does not compute the fusion expenditures, but indicates it is the middle per cent, we understand that it is the melted metal, that is, of 3000 Cs of 18 carat gold.

Units of Weight for the Gold	Monetary Units
1 marco = 50 castellanos = 8 onzas	1 doblon = 2 Cs gold (8385 Gr fine gold)
1 castellano = 8 tomines = 96 granos	1 doblon = 4 patacones
1 onza = 6 castellanos + 2 tomines	1 patacon = 1 onza silver (28,608 Gr silver)
1 onza = 8 ochavas	1 patacon = 8 reales
1 ochava = 6 tomines + 3 granos	1 real = 34 meravedies
1 marco = 228·86 gramos (sistema metrico decimal)	

Table II

Yields and Costs of the Second Refining

Gold obtained = 1504 castellanos of fine gold (1719 Cs 18 carat gold)
Value of this gold = 4329 patacones
Platina obtained = 325 Cs (We do not know its value but it might be worthless)
Cost of the nitric acid = (261 pounds) = 2349 patacones
Cost of manual labour and consumable = 145 patacones
Physical loss in weight = 569 Cs = 1031·3 patacones*

Total cost = 3525 patacones

* As we shall see in the balance of weights, he does not recognise this sum as a loss but he imputes it to platinum (in order not to recognise such physical waste); we evaluate this loss as referred to original alloy (it is an estimation) and therefore it is equivalent to 358 Cs of fine gold

The costs of the first refining operation, the repeated fusions stage, are shown in Table I. It can be seen that the cost of this part of the procedure is equivalent to 6.6 per cent of the value of the gold recovered.

The costs for the second part of the operation, that is the recovery of the gold from the 2900 castellanos of platinum-containing residue by the inquartation process, are given in Table II. These costs amount to 81.4 per cent of the value of the gold recovered!

The difference between the costs of the two refining stages is considerable; those for the first stage appear reasonable, while those for the second are clearly prohibitive. The most significant charge is for nitric acid, which amounts to 54 per cent of the value of the gold. When averaged over the whole yield, the total refining cost amounts to 36 per cent of the value of the gold recovered.

As we have noted previously, it was very fortunate for Sánchez that the platinum was not already alloyed perfectly with the gold. If this had been the case the extrapolated costs for treating the whole mass of alloy by inquartation would have risen to 7240 patacones, based on costs of 4826 patacones for nitric acid, 298 patacones for manual labour and 2116 patacones for process losses (735 castellanos of fine gold), so increasing the refining costs to 67 per cent of value of the refined gold.

These data provide ample justification for the attitude of the Spanish Administration in attempting to prevent, at all costs, the adulteration of gold with platinum. It did not signify, as has often been inferred, any lack of interest in the proper scientific investigation and exploitation of this new metal.

The act of throwing the platinum into the rivers can easily be justified. The cost to the Spanish Crown of the introduction of just 5.4 per cent of platinum into the gold alloy would be the value of 2515 castellanos of gold compared to 3750 castellanos of separation costs, and all for a fraudulent gain to the miner of just 325 castellanos. Under these circumstances, when the fraud was successfully achieved it would have been better to "turn a blind eye", in the knowledge that the normal cupellation assay methods would be unlikely to detect low levels of adulteration.

Where the platinum addition was high, the same result could be achieved by diluting its concentration by adding more pure gold. Nevertheless, the policy of dumping the platinum was reasonable in the sense of "avoiding temptation", particularly since platinum had no recognised value or uses in those days.

The balance of weights shown is somewhat confusing in that it is not a balance of physical weights. It is an accounting balance in terms of

the weights of 18 carat gold, this being the fineness of the first gold product obtained. This may have led Sánchez to make certain mistakes, or possibly even to make intentional falsifications so that the true gold losses were difficult to detect.

The first stage is clear, from the 5958 castellanos to be refined he obtained 3000 castellanos of 18 carat gold (which he called the "first benefit") and another 2900 castellanos of gold containing platinum, giving a loss of 58 castellanos. He inquarts the 2900 castellanos with silver in the proportion 1:4, so obtaining 290 Marcos (14,500 castellanos) of granulated silver-rich alloy, which he subjects to the separation process, and this is where the accounting problems begin.

Sánchez claims to have obtained 144,434 granos of gold; by implication pure gold, since he said that it made 2006 castellanos of 18 carat gold alloy. These are not physical weights, however, since what he actually obtained was 1719 castellanos of 21 carat gold alloy. These weights are all definitely self-consistent. From now on, in balancing the accounts he began to make mistakes. He used the calculated weight of 2006 castellanos to derive a figure of 894 castellanos for the loss, whereas he should have used the weight he actually had, namely the 1719 castellanos of 21 carat alloy. He then reduced the presumed value content of the loss by 25 per cent to refer the presumed content of the loss to 18 carat, which is a nonsense. He calculated a content of 64,366 granos (670 castellanos) as the waste and described it as "what is identifyed as platina". From the 894 castellanos he calculated the loss as 15 per cent of the original mass of 5958 castellanos, and refers to it all as platinum. This is unlikely, since it assumes no loss of gold, which is improbable considering the complexity of the operations.

On the other hand, he physically delivered only 325 castellanos of platinum and not 894, the difference being a real loss. The platinum in the original material would thus have been much less than 15 per cent.

It is apparent that Sánchez de la Torre had been able to achieve a balance of accountable material, which would not have been possible for the true physical items. Attributing all the loss to the "valueless" platinum enabled him to avoid admitting the gold losses, which would have been a serious matter and one for which he would have been held responsible. Saying that there were "894 castellanos recognised as platina" did not, however, stop him saying in the last paragraph of the report "I deliver 325 castellanos of calcined platina". The difference is unimportant, since it would have been much more serious to acknowledge equivalent losses of gold.

References

1 Antonio de Ulloa and Jorge Juan, "Relación Histórica del Viaje a la América Meridional", 4 vols., Madrid, A. Marín, 1748

2 W. Watson, "Several Papers concerning a new Semi-Metal, called Platina; communicated to the Royal Society", *Philos. Trans.*, 1750, 584–596

3 Luis Ulloa Cisneros, "Historia Universal", Publications of the Instituto Gallach de Librería y Ediciones, Barcelona, S.L., 1932, 6 vols.

4 Armando Espinosa Baquero, "Nuevos datos sobre el descubrimiento del platino y su metalurgia en la Nueva Granada en el siglo XVIII", *Quipu*, 1985, **2**, (1), 7–21

5 José Sánchez de la Torre y Armas, Manuscript: Archivo Nacional de Colombia, Minas de Tolima, Vol.5, folios 330–331

6 L. F. Capitán, "Separating Platinum from Gold During the Early Eighteenth Century: The Methods Used in Spanish South America", *Platinum Metals Rev.*, 1989, **33**, (2), 73–80

7 J. C. Chaston, "The Powder Metallurgy of Platinum", *Platinum Metals Rev.*, 1980, **24**, (2), 70–79

8 M. Morin, "La Platine, L'or blanc ou le huitieme Metal", Paris, 1758 (Avec approbation & Permission du Roy)

9 José Celestino Mutis, Informe sobre la Platina, June 15th 1774, Real Jardín Botánico de Madrid

10 Ramón de Manjarrés, "D. Jorge Juan y D. Antonio de Ulloa, La Medición del Arco Terrestre, La Historia del Platino (conclusión)", *Revista de Archivos Bibliotecas y Museos*, Tercera Epoca, January 1913, Madrid, 58–91

11 Expediente del Platino, Audiencia de Santa Fé, Legajo 835, Doc.3, Archivo General de Indias Seville

12 A. Galán and R. Moreno, "La Separación del Oro de la Plata. Un problema de la Metalurgia en la América Colonial", *Investigación y Ciencia*, 1992 (in press)