Separating Platinum from Gold During the Early Eighteenth Century

THE METHODS USED IN SPANISH SOUTH AMERICA

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Following the discovery of platinum in the Viceroyalty of New Granada at the beginning of the 18th Century, its use to degrade gold forced the colonial authorities to improve their existing methods of separating and analysing the precious metals. Using information from the Royal Mint of Santa Fé de Bogotá, the various ways of separating these metals are now considered, including the little-known method of inquartation.

Even before the discovery of the Americas by European explorers, elementary platinum metallurgy was apparently known to some of the indigenous population of the central region of New Granada; an area, shown alongside on a rare 18th century map, which was never fully integrated into the Inca world, and which now constitutes the southern part of Colombia and the northern part of Equador. Following the conquest of the New World by European invaders, however, this information appears to have been lost.

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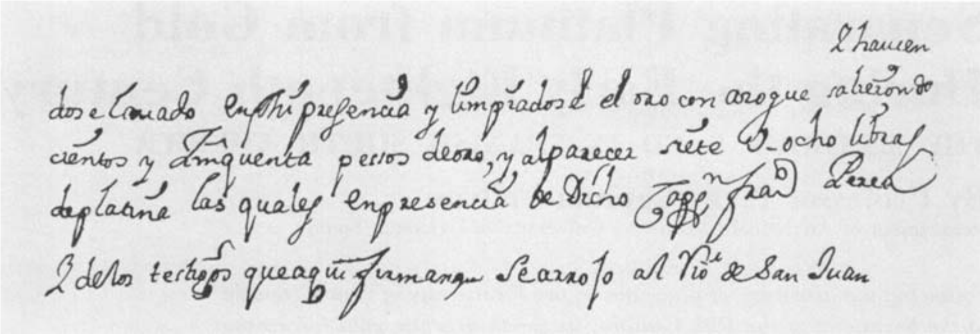
The somewhat late discovery of platina in the Chocó area of the New Granada viceroyalty, during the 18th century, was due to several factors. This area had remained relatively isolated from Spanish penetration because of the mountainous terrain, high temperatures, heavy rainfall, numerous rivers and, above all, warlike inhabitants. For these reasons, the extraction of Chocóan gold from placer deposits and gold-bearing veins did not begin until almost the 18th century, so it was only then that the existence of platina among the gold was recognised. Indeed the presence of platina in such an important gold mining region constituted a problem for both the miners and the colonial authorities.

However, platina could have been encountered as early as 1690, when the platiniferous area around Tadó in the upper part of the San Juan river valley was first worked. Its presence in the gold obtained from alluvial deposits would have been noted by the miners, by employees of the Nóvita and Citará foundries, and by officials of the Royal Mints at the administrative centres of Popayan, Mariquita and Santa Fé de Bogotá, where the gold was melted.

Soon gold was being degraded by the deliberate addition of platina, which was difficult to detect because of its similar density. Indeed the first written reference to platina noted that the mixing of platina and gold was banned (1).

This contamination required the colonial authorities to improve the existing methods of identifying platina and of separating it from the gold with which it occurred. Three methods were available: amalgamation, inquartation and


el hauer
dos e lauado en esta presencia y limpiado el oro con azogue sacaron dos
cientos y cinquenta pesos de oro, y al parecer siete u ocho libras
de platina las quales en presencia de dicho Joseph Juan Perea
y de los testigos que aqui firmaran se arrojo al Rio de San Juan

This is the first known account of the separation of gold from platina by the amalgamation process, and it forms part of a Tado judge's inquiry, dated 1721

melting. The inquartation method which was used at the beginning of the 18th century is not generally known today, although people are more aware of the other two processes.

The first information about platina to reach Europe was communicated by Antonio de Ulloa (1716–1795), in the famous "Relación Histórica" (2). This was written as a result of the French-Spanish geodesic expedition, whose objective was to determine the shape of the earth. Following this event, scientific investigation of platinum started in Europe in 1748, at least half a century after some technical knowledge of it had existed in New Granada.

The occurrence of platina in the Viceroyalty of New Granada at the beginning of the 18th century, the legal and technical problems that it caused and the solutions provided at that time are not well known today. Therefore in this article we will examine the methods used at that time for the separation of platina from gold in Spanish America.

Separation by Amalgamation

The amalgamation method of separation is based upon the fact that the solubility of the platinum group metals in mercury is low, while the solubility of gold is high. Platinum and palladium, the lower melting points metals in the platinum group, form intermetallic compounds with mercury. Both show slight solubility in mercury: 0.0008 and 0.2 weight per cent for platinum and palladium, respectively, at a temperature of 300°C (3); although higher figures have been suggested for platinum: 0.1 and 0.2 weight per cent at 24 and 54°C, respectively (4). The platinum group metals with the higher melting points, namely osmium, iridium and ruthenium, do not form intermetallic compounds with mercury as their solubility is very small ($<10^{-5}$ weight per cent at 500°C). Finally, rhodium shows a slightly higher solubility than these (6×10^{-5} weight per cent at 500°C), but it does not form compounds with mercury (3).

At the end of the amalgamation process, the amalgams and any remaining mercury are separated from the insoluble waste by filtration through leather or various types of cloth, the degree of separation being determined by the pore size of the filtering medium (5). Thus, the amalgamation process would be better for separating osmium, iridium, ruthenium and rhodium than for platinum and palladium. However, all of them would, to some slight extent, form an amalgam with mercury and would therefore be recovered with the gold.

In Spanish America treatment with mercury was the usual means of isolating gold mined from mineral veins. The process was not necessary for gold recovered from placer deposits, as Bernabe Cobo (1582–1657) noted in his "Historia del Nuevo Mundo" (6):

> "Gold is present in two forms: the first, pure and perfect, does not need to be melted nor treated by heat or mercury, and the second, in veins, like silver, is firmly embedded in the rock."

It was, however, necessary to demonstrate that alluvial gold which contained platina, could be purified by amalgamation.

In the Chocó area the amalgamation process was carried out in shallow wooden or clay washing pans or trays (bateas), where the finely divided alloy was treated with mercury. After that, it was separated by passing the amalgam through filter cloths.

The recovery of gold from the amalgam was carried out by distillation in an improvised furnace containing two different sized bateas, arranged one above the other. A very hot flagstone with the amalgam upon it, was placed inside the furnace and then the volatilised mercury condensed on the upper batea and collected in the lower one, while the resulting gold remained on the stone (7).

The first known reference to the use of the amalgamation process to separate gold from platina appears in a report dated 1721 (8). It occurs in an account of a Tadó judge's inquiry, in which he points out that he had been present during a separation operation:

> "The gold was washed and cleaned in my presence with mercury and gave two hundred and fifty pounds and what appeared to be seven or eight pounds of platina. The latter took place in the presence of Captain Francisco Perea and witnesses who hereby confirm that it came from the San Juan river".

On many occasions this amalgamation process has been quoted as being the only method used for the separation of platina before a scientific interest in the platinum metals developed in Europe during the second half of the 18th century (9). However, this was erroneous.

A Separation Method Based on Alloying

In the same way as gold, the platinum group metals are very resistant to chemical reagents, including acids, bases and halogens. This is due to the thermodynamic stability of their crystalline structures and also to the formation of monoatomic layers of some oxides on the surface of the metals during the dissolution process, which renders them passive (10).

Nevertheless, the reactivity of the platinum group metals is largely determined by their degree of dispersion in other metals, as well as by the formation of intermetallic compounds. It also depends on the presence and type of impurities, particle size, metallurgical history and dissolution technique employed.

Therefore, one way of breaking up compact metals before dissolution is to alloy them with a more active metal. In this way the dispersion of the platinum group metals throughout the metal, or the formation of intermetallic compounds which are soluble in mineral acids, helps the dissolution process (11, 12). To assist in the dissolution of the platinum group metals, zinc (13–16), tin (12, 17), bismuth (12) and silver (18–26) have been used.

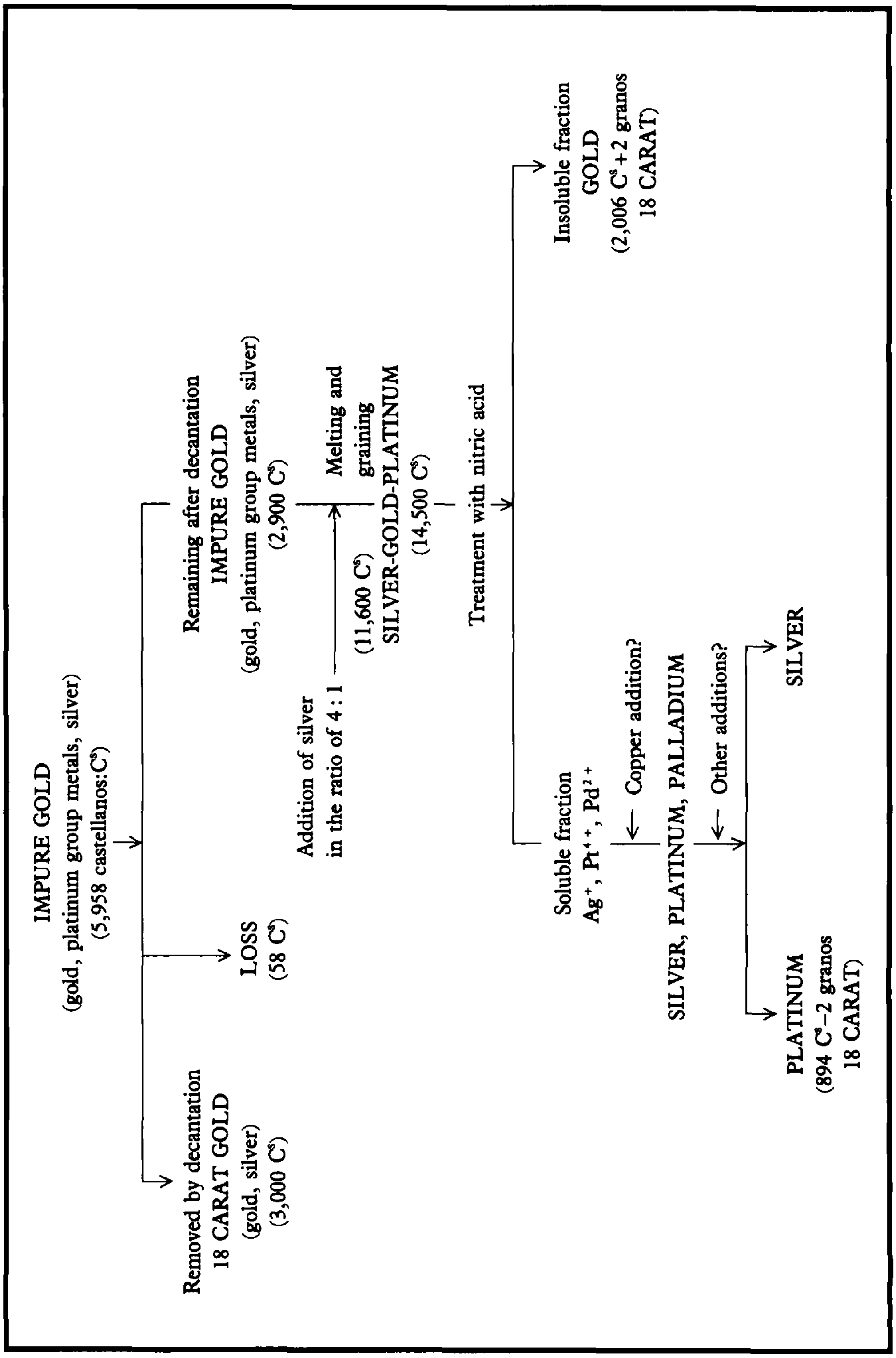
In the case being considered here, the separation is based on a ternary silver-gold-platinum alloy. In suitable proportions, this alloy is partially soluble in nitric acid which, of course, leaves gold undissolved. In consequence, the addition of the correct quantity of silver followed by treatment with nitric acid, will permit the separation of the gold-platinum alloy.

This method of separation, from now on referred to as the inquartation process, is very similar to the apartado method, which, during the time we are referring to, was used to separate gold and silver, and was based upon the selective dissolution of silver in nitric acid.

The Inquartation Method in Europe

The inquartation method of separating gold and platinum was investigated in Europe by several scientists. The first of these was the Frenchman Mathieu Tillet, (1714–1791), the Royal Commissioner for Assays and Refining at the Paris Mint, who in 1779 published three articles about this method (23, 24, 25). In these he said that a good separation will always be achieved if the metals are properly alloyed (which can be obtained by cupellation), if the proportion of platinum is low (0.1 to 0.05 of the gold), if the proportion of silver is high (two or three times the amount of the remainder), and if the nitric acid used is not concentrated.

Other authors including Vauquelin (26), Debray (27), von der Ropp (22) and Vèzes (28)


IMPURE GOLD
(gold, platinum group metals, silver)
(5,958 castellanos:C^s)
Removed by decantation
18 CARAT GOLD
(gold, silver)
(3,000 C^s)
LOSS
(58 C^s)
Remaining after decantation
IMPURE GOLD
(gold, platinum group metals, silver)
(2,900 C^s)
Addition of silver
in the ratio of 4 : 1
(11,600 C^s)
Melting and
graining
SILVER-GOLD-PLATINUM
(14,500 C^s)
Treatment with nitric acid
Insoluble fraction
GOLD
(2,006 C^s+2 granos
18 CARAT)
Soluble fraction
Ag^+, Pt^{4+}, Pd^{2+}
Copper addition?
SILVER, PLATINUM, PALLADIUM
Other additions?
SILVER
PLATINUM
(894 C^s–2 granos
18 CARAT)

also knew and studied this method, which is given in various books as the customary method of separation (18, 29, 30).

An Earlier Record by Sanchez de la Torre

Although usually attributed to Tillet, this method of separation was certainly used in Spanish America at least fifty-six years earlier. It was described in a short report dated 15th June, 1726 and signed by José Sanchez de la Torre y Armas, who was the assayer at the Royal Mint in Santa Fé de Bogotá, now known as Bogotá (31).

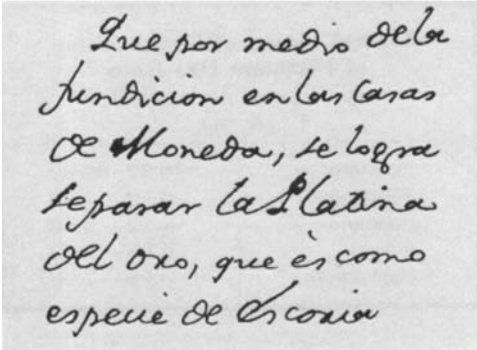
The note begins by stating its objective; in translation the text reads:

> "I, Don Joseph Sanchez de la Torre y Armas, Assayer at the Real Casa de Monda give notice of the gold which was handed over to me on behalf of His Majesty by the Royal Officers of this Kingdom in six bars mixed with platina, which weighed five thousand nine hundred and fifty-eight castellanos for the purpose of separation, which was carried out using the following method".

He then goes on to describe briefly how the separation was performed. The method employed was based upon the fact that in practice gold is not alloyed with the naturally occurring platinum complex, which remains dispersed throughout the gold (5). The method consisted of two basic stages, the progress of which is shown in the Scheme.

Separation by the Melting Method

Initial heating melted only the gold, because its melting point is substantially lower than that of platina. The platina-containing grains remained unaltered and, because their density is higher than that of gold, they sank to the bottom of the melting pot. Then decantation was used to separate the first portion of "clean" gold from the remainder. In this way the purified gold, amounting to about half the sample, was separated from the impure remainder (2900 castellanos), while 58 castellanos were lost during the process. The separation was not complete, however, because very small platina-containing particles would have remained in


Que por medio dela
fundicion en las Casas
de Moneda, se logra
separar la Platina
del oro, que es como
especie de escoria

The lower melting point and lower density of gold, compared with those of platina, formed the basis of a method of separation which according to this report dated 1766 was a usual method of separating these two materials

suspension in the gold, while others, containing a high proportion of ruthenium, may also have been present in the molten material due to their low density (5).

Consideration of the analysis shows that the composition of the "clean" gold separated out by this method was 18 carat. In the first place, this means that the original sample of impure gold containing platina was 18 carat, because only platina had been separated out during the fusion process due to its density. Secondly, it indicates that the 3000 catellanos were made up of 2250 castellanos of pure gold (24 carat) and 750 castellanos of perhaps silver or copper. We believe that this was most probably silver, because the next part of the procedure was generally used to separate gold from silver. So, melting could be considered as the third procedure for separating gold from platina. A report from the Viceroyalty of New Granada dated 1766 says:

> "by means of melting in the Mints, separate platina is got from gold as a kind of slag" (32).

The Original Inquartation Method

The second stage of the separation concerned the 2900 castellanos of impure gold remaining behind after decantation, and which contained the platinum group metals. The original composition of this material would have been approximately 52 gold, 23 platinum and 25 per

Typical Range of Composition of Platinum Ore from the Chocó Area, (38) per cent	
Platinum	76.82–86.20
Palladium	0.50– 1.66
Rhodium	1.22– 3.46
Iridium	0.85– 2.52
Osmiridium	0.95– 7.98

cent silver. Then the inquartation operation took place, involving the addition of silver in the ratio of 4:1. After melting and homogenisation the molten silver-rich alloy was poured into water, causing it to solidify as fine granules with a composition of 10 gold, 5 platina and 85 per cent silver.

These granules were then reacted with nitric acid which dissolved the silver and the platina, leaving the gold unaltered. The platinum group metals are not equally soluble, however, and probably only platinum and palladium would have dissolved in the acid, leaving ruthenium, rhodium, iridium and osmium undissolved; a more energetic action being required for their dissolution. However, when the composition of the ore from the Chocó region is considered, see the Table, this degree of separation is quite acceptable.

As noted above, a sufficient addition of silver, proper homogenisation and a suitable concentration of nitric acid were required for this stage in the process to be carried out satisfactorily. Sanchez de la Torre noted:

> "Four and a half pounds of aqua fortis are needed to separate five marks as the process required repeated washing on account of resistance towards separation or towards absorbing other platina, causing a new alloy to form in some grains when the platina has amalgamated and does not contain sufficient silver for the aqua fortis to have effect."

As a result of these operations the insoluble fraction consisted of 2,006 castellanos of pure gold and two granos considered to be 18 carat.

The Isolation of the Platina

The soluble fraction of the separation eventually yielded 894 castellanos of platina:

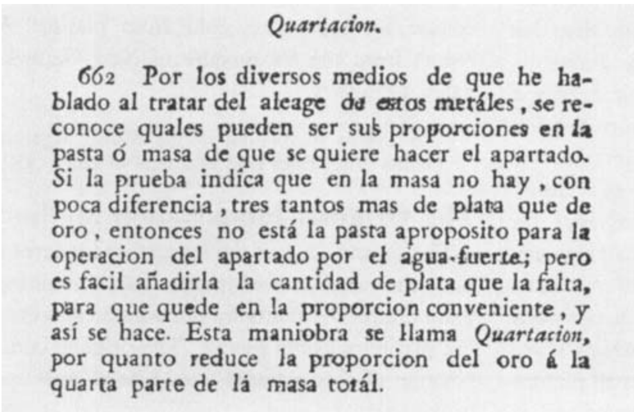
> "Such that the other five thousand nine hundred and fifty-eight castellanos of gold were reduced to fifty-eight castellanos of wastage and eight hundred and ninety-four castellanos of platina".

Referring to another separation, Sanchez de la Torre wrote:

> "It also produced three hundred and twenty-five castellanos of calcinated platina in grain, waste from that which was consumed by the aqua fortis during the separation process",

which suggests the possibility of a process to separate platina from silver in solution. However, nothing is recorded in the note about the technique.

One method could have been to precipitate silver and the platinum group metals together from solution using metallic copper. This was the system used to collect silver after it had been separated from gold in the "beneficio de apartado" (33). The mixture of silver and



Quartacion.

662 Por los diversos medios de que he hablado al tratar del aleage de estos metáles, se reconoce quales pueden ser sus proporciones en la pasta ó masa de que se quiere hacer el apartado. Si la prueba indica que en la masa no hay, con poca diferencia, tres tantos mas de plata que de oro, entonces no está la pasta aproposito para la operacion del apartado por el agua-fuerte; pero es facil añadirla la cantidad de plata que la falta, para que quede en la proporcion conveniente, y así se hace. Esta maniobra se llama *Quartacion*, por quanto reduce la proporcion del oro á la quarta parte de la masa totál.

This inquartation operation used to separate gold and silver (35) formed the basis of the method developed to separate platina

platinum group metals precipitated in this way could then be individually separated by treatment with nitric acid, after being melted and grained. This separation would be adequate, but not complete as some platinum and other elements would be dissolved in the nitric acid (34).

Another possibility could have been to separate the silver as silver chloride, and then to precipitate the platinum group metals with copper or another metal. This was the method used by Tillet many years later (24).

The Origin of Inquartation for Platina Separation

It is possible that the discovery of this inquartation method of platina separation could have been made by workers at the Royal Mint in Santa Fé. In any case the method was not well known; however, its origin can be found in the inquartation operation carried out to separate gold and silver by the "apartado" method. Ribaucourt said of inquartation:

> "The various methods I have mentioned for treating the alloy of these metals determine its proportions in the paste or mass which is to be separated. If the test shows that there is more or less than three times as much silver as gold in the mass, it is not suitable for the aqua fortis separation process; but it is easy to add the necessary amount of silver to make it up to the appropriate proportions and this is how it is done. This stage is called inquartation since it reduces the ratio of gold in the total mass to a quarter."(35)

In the separation we are considering here, a little more silver is added—four marks of silver to one mark of impure gold.

Errors in the Melting and Inquartation Methods

Several mistakes could possibly occur in the melting and inquartation methods of separation. If platina was alloyed with gold then it would not separate in the first "beneficio" by melting. Nevertheless only a very small amount would be involved, as there is little tendency for these elements to alloy. The same could happen with very fine grains of platina, which, as noted above, would not separate out by gravity but would be decanted in the "clean" gold.

We must also consider the fact that the dissolution of silver and platina by nitric acid is never complete. As has been said already, not all of the platinum group metals are soluble in nitric acid, indeed platina is not completely dissolved by this method either.

Tillet gave positive errors in the range of 0.3 to 1 per cent in the separation of platinum from the silver-gold-platinum alloy in which the platinum varied from 2.2 to 2.9 per cent (24). However, Vauquelin did not report errors if the platinum content was less than 5 per cent (30); interestingly, the proportion of platina in the inquartation alloy which was reported on by Sanchez de la Torre, was 5 per cent.

An Economic Comment

Using the costs given by Sanchez de la Torre it is calculated that the additional separation and purification processes required to remove the platina would increase the cost of gold by approximately 20 per cent (3 reales 12 maravedies is the cost of purification per castellano and 17 reales 4 maravedies the value of the gold purified). This, together with its illegal use to degrade gold, explains why platina was then regarded by the colonial authorities as a serious problem. Later of course the Spanish authorities made substantial amounts of metal freely available to European scientific institutions, so encouraging a continuing interest in the investigation and application of the properties of platinum and its allied metals.

Acknowledgements

The report by Sanchez de la Torre which has been examined here was also considered as part of the subject matter of an interesting earlier paper (36), the author of which drew somewhat different conclusions about the part that aqua fortis would have played in the separation process.

Thanks are due to the Instituto de Historia y Cultura Naval de España for their support during part of this investigation.

Footnote

The following units of mass were used in the original 18th century Spanish colonial documents. Conversion figures where known, are given (37). Pound = Peso = 460g, Mark = 230g, Castellano = 4.6g, Grano = 0.0648g.

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The Discoverers of Platinum Metallurgy

The early use of platinum as a jewellery material, and the methods by which it was fabricated by South American Indians has been considered here previously (*Platinum Metals Rev.*, 1980, **24**, (4), 147–157). These Indians occupied a coastal lowland area near the present-day cities of Tumaco and Esmeraldas, and examples of their work in platinum and gold were first recovered from burial mounds and cemeteries in the mid-19th century.

The dating of these objects has been difficult, but it has been suggested that by the early centuries of the Christian era the necessary platinum technology had been worked out. In a recent publication Warwick Bray recounts some of the archaeological discoveries made in this region of Colombia and Ecuador (*Américas*, 1988, **40**, (6), 44–49). Among the artefacts recovered from new excavations made by a French-Ecuadorian team at La Tolita was a scrap of sintered gold-platinum alloy sheet, and as a result of their discoveries the history of platinum metallurgy has been pushed back to the second century B.C., or perhaps earlier.