

Platinum —From exotic to commodity

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Platinum was brought to Europe in the middle of the sixteenth century and was soon recognized a true metal, which could not be fused. It remained an expensive curiosity for almost 200 years, until scientists learned its properties, how to melt it in large quantity, and discovered that four new elements, rhodium, iridium, osmium, and palladium, accompanied it (the platinum group metals). The early uses of platinum were in jewelry, laboratory ware, and coin manufacture. By the end of the nineteenth century a platinum-rhodium alloy was adopted for constructing the standard meter and kilogram. Production of platinum grew very slowly; it was only about one ton per year by 1911. The breakthrough came with the discovery of the extraordinary catalytic properties of the platinum metal group. Today these metals stand at the heart of the petrochemical industry and are the basis of all the means for controlling the emission of obnoxious gases of motor vehicles. Annual production has now reached near 190 tons.

Discovery

There is very little archeological evidence that platinum was known and used by ancient cultures. One of earliest indications is a gold etui dating from the seventh century, kept at the Louvre, which was found at the excavations at Thebes, Egypt. This box is covered with hieroglyphic inscriptions; on one of its sides it has gold characters while on the other side, of silver. Marcelin Berthelot (1827-1907) examined the latter and found it to be “d’un alliage complexe renfermant plusieurs des métaux de la mine de platine sans préjudice d’un peu d’or” (a complex alloy containing several platinum metals with a little gold)¹. According to Lucas², several Egyptian gold objects in the Cairo Museum, dating from the XII Dynasty, show numerous silver-white specks of platinum on their surface. Pliny in his *Historiae Naturalis*³ describes black heavy sand, which he calls *plumbum candidum or cassiteros*, which has been suggested, might have been platinum^{3a}. Georgius Agricola (1494-1555) does not mention platinum in his books; he coined the term *plumbum cinereum* for bismuth, no doubt following the Roman term for tin, *plumbum candidum* and knew only one tin material: “Lapilli nigri ex quibus conflatur plumbum candidum”, that is, little black stones from which tin is smelted⁴. In 1790, Father Angelo Maria Cortenovis (1727-1901) tried to prove that *electrum*, the white gold-silver alloy used by the Mediterranean people, and mentioned by Pliny^{3b}, was actually platinum⁵.

Information regarding the existence of an infusible metal in Mexico reached Europe as early as the middle of the sixteenth century. The platinum came from a relatively small area in the Choco district of what is now Colombia. The Spaniards named the metal as *platina del Pinto*, *platina* being a somewhat derogatory diminutive of *plata* meaning silver; *Pinto* is said to have been a river in the neighborhood of Popayan, in the gravels of which the substance was first distinguished. Most sources indicate that the first person to make Europe familiar with the name *platina* was Antonio de Ulloa (1716-1795). In his book about the French scientific expedition to measure the length of a degree of longitude at the equator he wrote⁶: “En el Partido del Choco, haviendo muchas Minas de Lavadero, como las que se acaban de explicar, se encuentran también algunas, donde por estar disfrazado, y envuelto el Oro con otros Cuerpos Metálicos, Jugos y Piedras, necesita para su beneficio del auxilio del, azogue, y tal vez hallan Minerales donde la Platina (Piedra de tanta resistencia, que no es fácil romperla, ni desmenuzarla con la fuerza del golpe sobre el Yunque de Acero) es causa de que se abandonen; porque ni la calcinación la vence, ni hay arbitrio para extraer el Metal, que encierra, sino a expensas de mucho trabajo y costo.” (In the district of Choco are many mines of *lavadero* or wash gold, like those we have just described. There are also some mines where mercury must be used, the gold being enveloped in other metallic bodies, stones and bitumens. Several of these mines have been abandoned on account of *platina*, a substance of such

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resistance that, when struck on an anvil of steel, it is not easy to be separated; nor is it calcinable; so that the metal enclosed within this obdurate body, could only be extracted with much labour and charge).

E. P. C. Meyer has challenged the claim that de Ulloa was the first to make the mineral familiar in Europe⁷. In a short note published in the journal *Science*, he reported that the Archivo General de Indias in Seville and the Archivo Histórico y Biblioteca Nacional in Madrid contain references to platinum dated 1735. Some of these refer to the shipment of rather large quantities (up to 18 pounds) of alloyed material, which was called platina. One document speaks specifically of refined platinum, which had been treated with mercury prior to its shipment to Spain. Meyer also mentions that the Indians regarded the substance as unripened gold, which they planted “back in the river bed to give it more time to ripen into the golden metal”.

The earliest known report of the existence of platinum in South America appears in a book by Julius Cesar Scaliger (1484-1558)⁸ where the author, repeating the definition that a metal is a substance that can be melted but when it cools remains hard, argues against it: “Besides we know that in Honduras, a district between Mexico and Darien (today Panama), there are mines which contain a metallic substance “quod nullo igni, nullis Hispanicis artibus hactenus liquescere potuit” (which it has not hitherto been possible to melt by fire or any of the Spanish arts). Thus, we see that the word melt cannot be applied to all metals”⁹.

In a letter to the editor, Paul Bergsøe¹⁰ reported that in La Tolita, Esmeraldas, Ecuador, prehistoric objects have been found to be made of gold alloyed with platinum. An interesting feature of these objects is that they have not been cast, all are either wrought or made from plate or wire; in addition the joints were made by welding. The pieces seem to have been melted on wood charcoal with the help of a blowpipe.

Another example is that reported in 1763 by William Lewis (1708-1781), a doctor of Kingston-on-Thames¹¹. He points out that a mineral mentioned by several authors including Joachim Becher (1635-1682) and George Ernst Stahl (1660-1734) under the name *Smiris Hispanica* (Spanish emery) seemed to have had many of the properties of platinum: “The smiris is said to be found in the gold mines and its exportation prohibited; to contain films or veins of native gold; to be in great request among

the alchemists; to have been sometimes used for the adulteration of gold; to stand equally with the noble metal, cupellation, quartation, antimony, and the royal cement; and to be separable from it by amalgamation with mercury, which throws out the smiris and retains the gold; properties strongly characteristic of platinum and which do not belong to any known substance.” Lewis also records a substance mentioned in 1640 by Alonso Barba (1569?-1661), a Spanish priest in the mining area of Perú. Barba wrote *El Arte de los Metales*¹² mainly about gold and silver. The work was important and kept secret in Spain, but the British Ambassador, Edward Montagu, Earl of Sandwich (1625-1672), managed to get a copy and translated it in 1669. In page 24, Barba refers to a stone called *chumpi* “que es una piedra de casta de esmeril, con participación de hierro, brilla algo oscuramente y es dificultoso su beneficio, por lo mucho que resiste al fuego. Hállase con metales negrillos y rosicleres en Potosí, Chocaya y otras partes” (*chumpi* is a hard stone, of the emery kind, participating of iron, of a grey colour shining a littler, very hard to work because it resists the fire much, found in Potosi, Chocaya, and other places, along with blackish and reddish ores that yield gold) Lewis believed that this particular mineral could be platinum only if were found in large masses, which it does not⁹.

In 1785, Jean-Baptiste Leblond (1747-1815) published a very detailed account of the occurrence and extraction of platinum in Peru. An interesting detail is that gold and platinum were separated from each other by hand, using a knife blade: “On les sépare ensuite grains par grains avec la lame d'un coreau ou autrement sur une planche bien lisse...”¹³.

Isolation and properties

The first platinum to be subjected to scientific investigation by European scientists was brought in 1741 from Cartagena (Colombia) to England by Charles Wood (1702-1774), described as an Assay Master of Jamaica and a “skilful and inquisitive metallurgist”¹⁴. On his arrival in England, Wood presented the specimens to William Brownrigg (1711-1800), a doctor practicing in Whitehaven, Cumberland. Brownrigg passed the samples on to William Watson (1715-1787) and asked him to communicate his findings to the Royal Society, which he did in 1749¹⁴. Wood did carry out some experiments and found that platina could not be melted at any temperature then obtainable even by adding to it borax or other saline fluxes. He noted,

however, that the Spaniards had managed to melt it “either alone or by means of some flux and cast it into sword hilts, buckles, snuff boxes, and other utensils.” Cupellation left the substance without alteration: “Having been melted in an assay furnace on a test with lead, and therewith exposed to a great fire for three hours, till all the lead was wrought off, the platina was afterwards found remaining at the bottom...without having suffered any alteration or diminution by this operation.” Watson found that platina was insoluble in nitric acid and soluble in molten gold. He was unable to confirm that its specific gravity was rather greater than that of gold as it had been rumoured, although some of his specimens had densities between 13.91 and 15. An equal weight mixture of gold and platinum had a density of 19. It was this last point that had given rise to the fear of the possibility of adulterating gold but further examination showed the risk to be limited by the fact that “upon a nicer examination the adulterated gold was found to be hard and brittle, and could not be separated from the platina and rendered ductile and pure, either by cementation, or by the more ordinary operations with lead and antimony”¹⁴.

Four years later, Lewis published an extensive memoir describing the chemical properties of the element¹⁵. The mineral as it arrived in England consisted of “a mixture of dissimilar particles, the most conspicuous and the largest part, are white shining grains, of seemingly smooth surface, irregular figures, generally planes with the edges rounded off. A few of them were attracted, although weakly, by a magnetic bar...the grains above described are the true platina”. The remaining material was composed of a number of mineral substances resembling the black iron sands found in other parts of the world. Also, noticeable was a little mercury or amalgam containing gold. From these observations, Lewis guessed the mineral had not been brought to England in its natural state but was the result of breaking large masses and treating them with mercury for the extraction of gold. Some of the grains of platinum could be flattened on the anvil by light hammer blows without breaking or cracking about the edges; others quickly cracked and exposed an internal granulated texture. The specific gravity of the original mixture was about 16.99; the platinum grains were separated by sieving, then treated with boiling aqua regia, sal ammoniac, and the purified metal recovered by strong heat. The resulting grains of platinum had a

density of 18.213. Lewis added the interesting observation that in them “the microscope still discovered a considerable portion of a blackish matter in their cavities.” When exposed to an extreme heat, the grains of platinum agglutinated into a mass, taking the form of the bottom of the crucible but they separated again under a moderate strong blow of the hammer; the grains were neither softened nor oxidized in any way. Platina mixed with borax, common salt, fixed alkaline salts, caustic alkali, calcium sulphate, calcium oxide, or different types of glass, and subject to an intense fire, did not change in any sensible manner.

Lewis described pure platina as a white metallic substance, malleable in a small degree, permanent to fire, indestructible by nitre, unaffected by sulphur, and soluble in *hepar sulfuris* (a mixture of various compounds of potassium and sulphur made by fusing potassium carbonate and sulphur). Platina was similar to gold, common acids did not attack it but aqua regia did. Hence, the common methods of gold purification with *aqua fortis* (nitric acid), *aqua regis*, or *regal cement* were no longer reliable in the case that this metal was adulterated with platinum. Platina melted with an equal weight of metals (tin, lead, silver, gold, copper, and iron) making them stiffer and harder. It also alloyed^{11,15} with mercury, bismuth, zinc, and antimony^{11,15} [The first paper by Lewis was translated into French by M. Delalande and published as a letter to the editor in the *Journal des Sçavants*, 1758¹⁶].

Lewis’s most important discovery was that the addition of ammonia to an aqua regia solution of platinum “precipitated a fine red sparkling powder which became blackish after being dried and exposed to heat in an iron ladle (this product would be later called sponge platinum), without at all fulminating, which calxes of gold, prepared in the same manner, do violently.” Water dissolved most of the precipitate, leaving only a small amount of solid blackish material. The filtrate had a bright golden colour originating from a small amount of powder passing through the filter. Lewis believed that the only way to make platinum malleable was by alloying it with another metal. Thus, he examined the properties of the alloys of platinum with tin, lead, silver, gold, copper, and iron and found that all of them, when digested with aqua regia, left several grains of platinum in their original form. Microscopic examination of the same showed that some appeared to have suffered no alteration while others exhibited a

very large number of small globular protuberances. Lewis also studied the properties of alloys of platinum with bismuth, zinc, mercury, antimony, and brass. Except for gold, the metal was easily separated by the action of simple acids. Mercury was the only one separable by fire.

At the request of the Spanish Minister of the Indies, William Bowles (1705-1780) examined a sample of native platinum from South America and reported as follows¹⁷: "The grains of platina then resembled lead shot, still more the semi-metal which the Germans called speiss, which is a regulus of cobalt often included in saffre. The weight of platina surprised me because it exceeds that of 20 carat of gold...In remarking that the sand was only malleable to a certain extent I wished to try to melt it in a furnace which a very clever Swiss used for the separation of gold by the dry way. The fire was so violent that it melted a part of the crucible and the grains of platina united themselves in a group without any loss of colour or sign of true fusion, after two hours of the most lively fire...I thought that the platina may contain some portions of true sand and that this would be vitrified by the phlogiston of the metal. To convince myself I washed a little of the platina and put it in another crucible glazed with common melted salt. After three hours nothing had melted but the grains were not so strongly united as in the first time, several even remained separate." Bowles also noted that light hammer blows easily separated the grains of platina that had been joined by the action of heat. The metal was not attacked by sulphuric acid or nitric acid, and slightly by hydrogen chloride. Platina alloyed with lead and the components could be separated with nitric acid, leaving a black residue⁹.

The earliest German work on platinum was carried out by Andreas Siegmund Marggraff (1709-1782)¹⁸ who repeated some of the experiments done by others and again observed that at a very high temperature, platinum grains only sintered together and were easily broken up by hammer blows. He also found traces of mercury in the raw material and assumed they originated from an amalgamation process. Hydrogen chloride dissolved the accompanying iron while aqua regia dissolved the platinum itself. Treatment of the resulting solution with copper, iron, tin, lead, mercury, zinc, or antimony precipitated the metal together with the platinum. Marggraff remarked that a solution of platinum in aqua regia, which deposited red crystals on evaporation, gave no precipitate with

solutions of mineral fixed alkali (soda) but a yellow precipitate with a salt of tartar (potassium carbonate). He particularly emphasized that, the solution did not precipitate a solution of lead in nitric acid, which was peculiar since the acid of common salt exists in the aqua regia. He cupelled some of the yellow precipitate with lead and obtained "a rough, grayish and very brittle button, which was exactly like that obtained when ordinary platina was cupelled with lead." He repeated the experiment using sal ammoniac as the original precipitant and obtained similar results. The same result was obtained when the platinum solution in aqua regia was evaporated to dryness. He then ignited each residue, cupelled it with lead and noted that in each case the cupelled button always contained some lead. Next, he alloyed a similar button with some pure gold and an excess of silver and separated the components by addition of nitric acid. He found that in the course of this operation the platinum disappeared, the final residue being only the right weight of fine gold^{9,18}.

Platinum was little known in France until the year 1758, when Morin collected, translated into French, and published an account of all that hitherto done¹⁹. This publication initiated intense research, as will now be described.

In 1757, Antoine Baumé (1728-1804), received about a pound (*une livre*) of platinum from José Ortega y Hernández (1703-1761), Apothecary to the King Fernando VI of Spain, secretary to the Royal Academy of Medicine of Madrid since its foundation in 1734, and a corresponding member of the Paris Academy. Baumé and Macquer joined forces to make a physical and chemical study of the metal, particularly since Macquer owned some of the best furnaces constructed at the time²⁰. Macquer and Baumé observed that calcination of the raw mineral led to an increase of its weight and the appearance of a friable gray material, facts that suggested that the platinum was contaminated with a base metal, probably iron. Although they were able to remove most of the impurities by cupellation with lead in a high-temperature porcelain oven at the porcelain works in Sèvres, they failed again in their efforts to melt the metal. After many fruitless attempts to melting it using a variety of techniques, they came upon the idea of heating a small portion in the focus of a burning mirror (concave spherical mirror, *miroir ardent*), a method that no one had tried before. The mirror they used belonged to the Abbe Bouriot; it was

made of silver glass, 22 inches (*pouce*) in diameter and with a focal length of 28 inches. With this mirror they were able to melt the metal in five or six places; the liquid globules produced, remained attached to the mass and solidified as soon as they were moved out of the focus of the mirror. Macquer and Baumé remarked that while being heated platinum first smoked, then emitted sparks and the parts that melted were those exposed to the center of the focus. These were distinguishable from the other by brilliancy like that of silver and by a rounded, shining, polished surface. The platinum was found to be malleable; it was easily flattened upon an anvil and formed into very thin plates without cracking or splitting. It work-hardened like the other malleable metals and annealing could relieve this hardening. Purified platinum was not attacked by sulphuric acid, hydrogen chloride, or nitric acid; it could only be dissolved with boiling aqua regia, the best composition being equal weights of nitric acid and hydrochloric acid. About one pound of aqua regia was needed to dissolve one ounce of the metal because the rate of evaporation of the acid was much faster than that of dissolution of the metal. The reaction was very slow at room temperature but at the boiling point of the acid it became violent. At the beginning of the dissolution the liquid had the colour of a gold solution and then changed to a strong red and brown. According to Macquer and Baumé, the change in colour was only due to a concentration of the yellow colour.

The dissolved platinum could be precipitated from the solution with vegetable fixed alkali (potash) and volatile alkali (ammonia). Macquer and Baumé found that the colour of the precipitates varied from bright red through all shades of orange to pure yellow. Macquer believed that this change depended on the strength of the solution, while Baumé felt that it was due to the excess or otherwise of the base. Macquer and Baumé thought that the colours originated from a large quantity of saline material, which precipitated with the platinum and not from any calcinations of the metals "or loss of phlogiston", as shown by the fact that exposing the precipitate to strong heat platinum recovered its original colour. After precipitating the dissolved platinum with sal ammoniac they attempted to melt the precipitate (ammonium chloroplatinate) using a flux composed of borax, potassium tartrate, and white glass and found that the result, which at first looked like fusion, was really nothing more than

an agglutination of the particles, the product being quite brittle and not malleable. Macquer and Baumé, considered that the mechanical properties of platinum coupled to its resistance to air, water, and most reagents made it an ideal material for making burning mirrors, telescope mirrors, and vessels for the kitchen and the chemical laboratory. They mistakenly thought that "ce metal ayant la gravité spécifique de l'or & resistant à toutes les mêmes épreuves, pouvoir, par son alliage servir à des fraudes d'autant plus dangereuses...(that a metal having the same density of gold and passing all the tests for the same can be alloyed and be used for dangerous frauds..)"²⁰. Eventually Baumé showed this result to be erroneous and that platinum was more dense than gold and hence it would not be used as an adulterant²¹.

According to Smeaton²² Baumé evidently carried out further research alone because in his book *Chymie Experimentale et Raisonnée*²³, he reported that cupelled platinum could be forged by hammering, without the addition of another metal. Baumé wrote: "So many excellent properties united in a single metal make it desirable that it should be introduced into commerce. There is every reason to believe that it will possible to derive very great benefits from its use in an infinity of utensils, which made out of this metal will not be susceptible to attack by any kind of rust. For example, I have noticed that it submits to forging and welding like iron, without the introduction of any other metal. I have taken two pieces of platinum which have been cupelled in a Sèvres furnace; I have raised them to a white heat in good forge; having placed them one on the other, and struck them with a sharp hammer blow, they have welded together just as well and solidly as two pieces of iron would have done. This property of platinum of being malleable when hot and being capable of welding in that state, leads one to hope for the greatest advantages by treating it in this way when one cannot reach finality by fusion. The case of platinum would then be the same as that of iron, with which all kind of work can be done without our being obliged to melt it. It will be sufficient to melt this new metal a single time, either alone or by means of lead or bismuth, and subsequently to destroy these metals in the manner we have described above."

This observation of Baumé's and the conclusion that he drew from it were responsible for the start of the fabrication of platinum for commercial uses and

underlie the industry that gradually grew up during the next hundred year⁹.

Although Macquer and Baumé, as well their predecessors Lewis and Marggraff, were fully satisfied that platinum was an individual metal, there were other important scientists such as George Le Clerc, Comte de Buffon (1707-1788), Louis-Bernard Guyton de Morveau (1737-1816), and Nicholas Christien de Thy, Comte de Milly (1728-1784), who believed that this was not true, that platinum was actually an alloy of iron and gold. Eventually this idea faded away with the work of Torbern Olof Bergman (1735-1784).

It has been mentioned already that there was conflicting experimental evidence on the action of mineral fixed alkali (soda) on the solution of platinum in aqua regia; some claimed having observed precipitation, other the opposite. Bergman did a thorough study of the question and found that while small amounts of potash or ammonia were capable of precipitating the acid solution, large quantities of soda were needed for the same purpose²⁴. He believed that the precipitate produced by sal ammoniac in a platinum solution was a triple salt containing the constituents of sal ammoniac as well as platinum (true, it is ammonium chloroplatinate, $(\text{NH}_4)_2[\text{PtCl}_6]$). The colour of the crystalline precipitate obtained by adding to the acid solution, potassium or ammonium carbonates, varied from red to yellow, depending if the solution was concentrated or diluted, an observation that remained unexplained for twenty five years, until iridium had been discovered. Bergman found that ammonium chloroplatinate melted easier than the native metal. He also reported the specific gravity of the metal to be about 18⁹.

Antoine-Laurent Lavoisier (1743-1794) may be considered to be the first to actually achieve the fusion of platinum, which he did by directing upon it a stream of oxygen and hydrogen. Fusion was complete; the small particles of the metal were united in a perfectly round globule. Lavoisier also showed that the raw material was not a pure metal but contained an appreciable amount of iron, which had to be removed if the platinum was to be used. Removal could be done by dissolution with aqua regia followed by precipitation with sal ammoniac^{9,25}.

Jean-Baptiste Romé de l'Isle (1736-1790) also realized that before working on platinum it was necessary to remove the sand and the alloyed iron, which he did, following Lavoisier's

recommendations. Balthazar-Georges Sage (1740-1824) describes Romé de l'Isle's procedure as follows²⁶: "Sal ammoniac dissolved in the cold in distilled water is poured into a solution of platinum made by aqua regia; there is a reddish precipitate composed of platinum and sal ammoniac...this precipitate of platinum, exposed to a violent fire, melts and produces a button of malleable platinum of whitish-grey colour resembling that of silver, and which does not alter in the air"^{9,26,27}. Louis-Bernard Guyton de Morveau repeated Romé de l'Isle's work and found that reducing fluxes (glass, borax and charcoal) never yielded a malleable metal, although they led frequently to real fusion into beads. Better results were obtained by heating the sal ammoniac precipitate alone in a crucible, as originally recommended by Romé de l'Isle. The specific gravity of the material forging it was 10.045 and increased to 20.170 after forging. According to Guyton, the more malleable the metal, the less it was attracted by the magnet²⁸. Macquer understood clearly what was happening in the process, in his *Dictionnaire de Chimie*²⁹ he wrote: "...solid masses result which have all the appearance of quite dense material, melted and solidified by cooling, but they are really nothing but the result of a simple agglutination among an infinite number of infinitely small particles and not that of a perfect fusion as with other metals."

In 1752, Heinrich Theodore Scheffer (1710-1759) made the important discovery that addition of a small amount of arsenic to a much larger quantity of platinum brought its complete fusion at relatively low temperatures³⁰.

An important development in platinum technology was development of the technique for converting the alluvial deposits into platinum sponge, which could then be satisfactorily formed by heat into compact platinum or platinum artifacts. Franz Karl Achard (1753-1821) heated a mixture of platinum with arsenic and potash and obtained a metallic button, which when heated in a muffle to red heat released the arsenic in the form of white fumes. The solid remaining after the fumes had ceased was fully malleable and ductile as gold. Achard understood that this procedure allowed manufacturing "all kinds of small vessels and especially small fusion crucibles which can be useful in certain operations"³¹. With this discovery goldsmiths began to use platinum, first in small creations and then in larger ones, such as coffee pots, long bars (19 feet long), and heavy balls (144 ounces)⁹.

The arsenic procedure was used by Alexis Marie Rochon (1741-1817) to produce the platinum crucibles needed in the construction of his reflecting telescopes³². These crucibles, capable of containing 30 pounds of flint glass, were strengthened by covering them on the outside with a one-inch thick case of cast iron⁹.

Jan Ingenhousz (1730-1799) studied the physical properties of platinum, particularly its magnetism³³. He found that every platinum particle was a magnet; floating them on water and applying "magnetical bars" led to a change in the poles. In the course of this work he filled a narrow glass tube with platinum particles and subjected the contents to "five or six electrical explosions from three very large jars." Examination of the contents showed that the platinum was no longer magnetic and that particles appeared now as one uninterrupted cylinder of metal, with all the interstices filled with bright metal. Ingenhousz concluded that platinum was fused by "electrical fire" the same as iron. In addition, he found that the particles, which had not melted were more magnetic than before, so that although platinum lost its magnetic properties when heated, it recovered them when subject to an electrical discharge. Ingenhousz can then be considered the first to melt platinum by a means other than a burning glass³³.

As mentioned above, many scientists had noted that the precipitates of platinum chloride with ammonium or potassium chloride presented different colorations but these were not always yellow as expected. Antoine-François Fourcroy (1750-1809) and Louis Nicolas Vauquelin (1763-1829) investigated the residue left by the action of aqua regia on native platinum ore and found that it precipitated as a red platinum chloride. From these results they concluded that it contained a new metal: "Tout annonçait que le poudre noire contenait un metal nouveau (Everything points out that the black powder contains a new metal)^{34,35}. This statement was also reinforced by the findings of Hyppolyte Victor Collet-Descotils (1773-1815) who had stated that the colour of some salts of crude platinum were due to a new metal, which he did not isolate (iridium). In his research Collet-Descotils also examined the metal found with native platinum, which has "une grande résistance à l'action des acides" (has a great resistance to the action of acids) (now called osmiridium)³⁶. Vauquelin³⁷ and Fourcroy and Vauquelin^{34,35} also confounded iridium and osmium, ascribing both to a

single metal they called *ptene*. Smithson Tennant (1761-1815) separated and identified these elements in 1804³⁸.

Tennant decided, "to experiment on the black powder, which remained after the solution of platina and I observed that it did not, as was generally believed, consist of plumbago, but contained some unknown metallic ingredients"³⁸. He was aware that Collet-Descotils³⁷ and Vauquelin³⁶ suspected the presence of only one new metal in the black powder, but Tennant believed "that it contains also another metal, different from any hitherto known." He analyzed the material using a method similar to that employed by Vauquelin, namely, "the alternate action of caustic alkali and of an acid": the powder was mixed in a crucible of silver with a large quantity of pure dry sodium hydroxide, kept in a red heat for same time, and then washed with water. The alkali solution had a deep orange or brownish-yellow colour. The remaining powder was now digested with hydrogen chloride giving a dark blue solution, which then became dusky olive green, and later, on continued heating, attained a deep red colour. According to Tennant, the alkaline solution contained the "oxide of a volatile metal, not yet noticed and also a small proportion of the second metal." The volatile oxide could be separated by acidification and distillation. It was a colourless body, condensing first to an oily liquid and then solidifying into a semi-transparent mass. In all stages it had a strong and very characteristic smell. It was this that led Tennant to name the metal *osmium*, from a Greek word meaning smell. With regards to the other metal, Tennant's work confirmed and extended the observations of Vauquelin and Fourcroy^{34,35} on the subject and led him to name the second element *iridium* "from the striking variety of colours which it gives while dissolving in marine acid." Tennant's publication also reports his experiments on the properties and reactions of iridium, osmium and osmium oxide³⁸.

William Hyde Wollaston (1766-1828) studied the solution of native platinum in aqua regia using a similar procedure as that of Tennant, but directed his attention to the liquid phase remaining after the addition of sal ammoniac. He first neutralized the solution with soda and then introduced in it bars of iron to recover the dissolved platinum, as well as other substances which he believed were present. The new precipitate was a fine, very black powder. He suspected that something new was present in it,

remaining in the solution after the precipitation of platinum by sal ammoniac, which was neither platinum nor Tennant's iridium. He soon came to the conclusion that a new metal was present, which he called *palladium* after the asteroid Pallas that had just been discovered by Heinrich Wilhelm Olbers (1758-1840)^{9,39,40}. Wollaston's discovery completed the identification of all the platinum group metals.

By 1810, the process invented by Wollaston became established: First, gold was removed by dissolving the raw material in aqua regia, then the excess acid was boiled off. The dissolved platinum was precipitated as ammonium hexachloroplatinate, and the gold chloride separated by washing. The remaining solid was calcined yielding platinum sponge. Metals such as iron, copper, and manganese, were removed by treating the metal grains with strong nitric and hydrochloric acids alternatively until the base impurities were removed. The platinum was then re-dissolved in aqua regia, precipitated with ammonium chloride, and reduced by gradually raising the temperature to red heat. To prevent precipitation of the other metals of the platinum group, the solution in aqua regia was freed as much as possible from excess acid, and nitric acid was added before precipitation with ammonium chloride. The platinum black, or powder obtained in this manner was pressed and beaten into sheets.

Wollaston used his procedure to manufacture crucibles and other laboratory ware by means of special moulds into which the powder was rammed. The moulds were then heated in an air furnace, subsequently in a very hot blast, and finished off on the anvil. He manufactured very large boilers of platinum capable of holding 300 pounds of sulphuric acid and showed that extremely fine wires of platinum would be drawn inside a silver sheath, and the silver afterwards dissolved off in dilute nitric acid^{41,42}.

The development of the manufacture technique and processing of the metal led, in 1817, to the formation of Johnson, Mathey & Co, London, which laid the foundation of modern technology.

In 1827, Jöns Jacob Berzelius (1779-1848) received a one-half pound of platinum mineral from the Urals, as a gift from Count Egor Frantsevich Kankrin (1775-1845) with the request that he analyze it. Berzelius began an intensive study of the platinum metals and a year later published an extensive paper on the platinum metals, their salts and double salts, and their atomic weights. In addition, he worked out a

precise method for the analysis of platinum ores and applied it in testing the samples of ores forwarded to him. Berzelius reported the following values for the atomic weights^{43,44}:

Element	Berzelius	Today
Osmium	198.94	190.2
Iridium	196.7	192.22
Rhodium	104.31	102.9055
Palladium	106.22	106.4
Platinum	197.10	195.09

The small concentration in which platinum metals were present and the high price of the raw material were for long, an obstacle for their serious study. The metals were separated in small quantities in very impure form and found to resist without melting, the temperature of the hottest furnaces. The properties of the material were extremely variable and depended on the mineral employed for their preparation. Of the six metals present, three were very heavy, platinum, iridium, and osmium, having densities of 21.46, 22.38, and 22.44, respectively. The three others, palladium, rhodium, and ruthenium, had density of 11.4, 12.1, and 12.16, respectively. All were attacked with difficulty by different reagents⁴⁵.

It took four years of hard work by Henry Sainte-Claire Deville (1818-1881) and Henri Debray (1827-1888) to develop a dry route method of analysis, appropriate for both the platinum mineral and the residues, which accumulated in the industries where these materials were treated. They also measured new properties of the isolated metals, or rectified previous ideas, which they proved were wrong. For example, osmium prepared by Berzelius had a density of 7; Deville and Debray showed that the actual density was 22.44, the highest of all known bodies. In addition, when osmium was heated in air beyond the fusion temperature of zinc, it burned giving off vapours of osmic acid, highly smelly and toxic. This acid could be kept indefinitely under vacuum; it was easily reduced by organic matter, particularly nervous tissue, thus justifying its use as an indicator in histological research. It melted at 40 °C, boiled at about 100 °C, and appeared as vapour whenever osmium-containing materials (except iridium osmure) were treated with aqua regia. In this manner, it was possible to eliminate it completely from the mother material⁴⁶.

In 1857, Deville and Debray devised a simple apparatus for melting platinum in quantity. This

consisted merely of two cylindrical blocks of lime bound with steel trip, each hollowed out in a saucer-shaped depression so that when they were placed one over the other, the two saucers formed an enclosed space in which solid platinum could be placed and melted by means of a coal gas-oxygen flame introduced through a hole in the top. The whole block could be tilted and the molten metal poured out through a hole in the side⁴⁷.

In his laboratory, at the *École Normale* Deville taught the art of purifying and melting platinum to many of his visitors. The bar metals that were prepared served as the kilogram and meter standards to many countries in the world; the patrons differed one from the other by no more than one-thousandth of a millimetre (see below).

Deville and Debray also developed a method for the complete separation of iridium from platinum. It was sufficient to melt the alloy of iridium and platinum with lead, which dissolved it; during cooling iridium crystallized first and platinum solidified afterwards. In order to study these two metals, which the most powerful metallurgical furnaces were unable to melt, Deville and Debray utilized the large heat released by the combustion of hydrogen or illuminating gas with oxygen. With the apparatus they developed for this purpose, they were able to melt 10 kg of platinum in less than 40 min. This procedure was also used to prepare alloys of platinum with iridium, and rhodium, which had several properties quite different from pure platinum.

An interesting epilogue is that Michael Faraday added a lecture of platinum to his famous series of lectures on the chemical history of the candle. This lecture is essentially a detailed account of the work done by Deville and Debray⁴⁸.

Coinage

It was known that in the Ural, particularly at Nijni-Tagilsk, there were platinum sands capable of yielding up to one gram of platinum per 15.5 kilograms of sand. The Russian government had employed platinum for several years in the fabrication of coins. In this mint about 14250 kilos of platinum were employed. Eventually, after the discovery of large quantities of platinum in other regions of the world, it was found that the ratio of the value of platinum to that of gold, fixed at the origin, was substantially higher than their market value. Hence, it was advantageous to introduce into Russia forged coins and obtain substantial profits. The resulting

fiscal loss led the Russian government in 1843 to withdraw platinum coins from circulation, mainly because the difficulty of minting them resulted in a considerable cost of manufacturing. In addition, these coins were looked down in commerce, and since the price of platinum was so variable, it was hard to assign them a constant value. The withdrawal left the Russian government with a stock of over 14 tons of coin metal, as well as significant amounts of residues very rich in platinum and iridium. All these led to a substantial decrease of the annual production of platinum, from about 1640 kg to less than 650 kg. Production grew again in 1858 when the price of platinum started increasing because of the return of the idea of mining coins because in the interim, a large amount of platinum had accumulated at the Mint in Saint Petersburg. The commission appointed to evaluate this possibility recommended against the idea and, as a consequence, the platinum of industry was declared free, without obligation of selling the material to the government for its refining⁹.

Since the then available methods did not permit the recovery of platinum, the Russian government approached Deville with the request that he study in a large scale the procedures he had developed for treating platinum minerals. Russia financed the construction of large-scale gasometers and reverberation furnaces, which were installed at the *École Normale* and at the end of the research project, were donated to the *École*. Deville and Debray were provided with 32 kg of mineral from the Urals, 16 kg of platinum from coins, and 8 kg of raw iridium; in total, 56 kg of raw material containing 42.2 kg of platinum. With this opportunity Deville and Debray were able to show in a large scale the economical value of their procedure. Within three months they produced the metal in different forms, ingots, thin plates, wire, etc., with a total weight of 42.080 kg, representing a loss of only 120 g due to the many operations they had performed. Enthusiastic by these results all the platinum manufacturers in Paris and London promptly adopted the procedures developed by Deville and Debray.

The standard meter

In 1867, a Great International Exhibition took place in London and during it discussions were held concerning standard weights and measures. The discussions were supported by the needs expressed by several learned societies such as the *Académie des Sciences*, *Association Géodésique*, and the *Saint*

Petersburg Academy of Sciences, regarding the manufacture of new standards and the precise determination of their value in the metric system. At the International Geodetic Conference held in Berlin the same year it was recommended to create an international bureau of weights and measures. A Committee of Weights and Measures was formed, of which most of the foreign scientists became members. In 1869, Boris Semyonovich Yakoi (1801-1874), the then President of the Academy of Sciences of Saint Petersburg, drew a report on the subject in which he recommended the appointment of an international commission of specialists to supervise the preparation of new standards. In response to all these requests, in 1870 the French government convoked the *Commission Internationale du Mètre*. The establishment of the International Bureau of Weights and Measurements was sanctioned by the *Conférence Diplomatique du Mètre* held in Paris in 1875. In the same year, the *Convention du Mètre* adopted the French system of weights and measures. In order to bring it into practice, it was necessary to select a metal able to provide the prototypes of the meter and kilogram, being the less sensible to mechanical action, to atmospheric agents, and capable of supporting without melting, the high temperature to which it might accidentally be subjected. The properties of the platinum-iridium alloy developed by Deville and Debray made it particularly appropriate for this purpose (high density, high melting point, great resistance to humidity an air, a fine grain, perfect polish, great hardness, and full malleability) and it was thus adopted⁹.

After this Deville had the difficult task of preparing in a state of very high purity the large quantity of platinum and iridium that was necessary for manufacturing the prototypes required by the signatory nations, to test alloys of different compositions, study their properties, and later on, to prepare the alloy that was finally adopted (containing 90% platinum and 10% of iridium). Not only that, they had to verify its composition, eliminate from the fabricated pieces the impurities introduced by the different fabrications steps, and finally, to bring all the prototypes to a common state of homogeneity. The standards prepared by Deville were incredibly accurate, the meter ones differed by no more than 1/1000 millimetre, and the kilograms by less than 1/100 milligram. One of the most serious problems they had to solve was the inevitable appearance of

puffs when manufacturing large ingots. These puffs appeared at the time of solidification of the metal, particularly because of the sudden release of the dissolved gas, retained as bubbles. The procedure selected was to submit the metal to strong mechanical compressions, until a satisfactory density was achieved.

Catalysis

In 1817, Humphry Davy (1778-1819) published a paper in which he described his accidental discovery of the fact that coal gas and air in contact with a hot platinum wire combined without flame and that this phenomenon occurred at a temperature well below that of ignition⁴⁹. The same result was obtained when the coal gas was replaced by ether, cyanogen, alcohol, oil of turpentine, and naphtha, and also when using palladium instead of platinum. Davy suggested that his discovery could be used to build a non-explosive lamp to be used in mining operations. Three years later, Edmund Davy (1785-1851), the discoverer of acetylene, reported that boiling a mixture of platinum sulphate with alcohol or ether precipitated a black substance in a finely divided state. Heating the powder produced a feeble explosion accompanied by a flash of red light and reduction of the platinum. Davy studied the properties and reactions of the powder and came to the conclusion that it was composed almost exclusively by platinum. An important reaction was the complete oxidation of alcohol to acetic acid⁵⁰.

As stated by Prandtl⁵¹, Johann Wolfgang Döbereiner's (1780-1849) most famous discovery came from his interest in platinum, which was fuelled by the discoveries made by Humphry and Edmund Davy. In 1821, Döbereiner repeated their experiments and found that platinum black not only oxidised alcohol to acetic acid completely but also remained unchanged by the reaction. This finding suggested the possibility of using the material for the direct production of vinegar from alcohol^{52,53}. In 1823, he showed that directing a stream of hydrogen on black platinum powder at room temperature resulted in the instant combustion of the gas. This important discovery led in 1824 to the manufacture of the famous Döbereiner lamp. In this apparatus, hydrogen produced from zinc and sulphuric acid passes through a jet and impinges on some spongy platinum suspended on a thin platinum wire. The gas catches fire and the flame can then be transferred to a candle. The *Döbereiner Feuerzeug* (Döbereiner lamp) was

used for lighting purposes for about 100 years until replaced by the phosphorus match. In 1832, Döbereiner discovered that sulphur dioxide can be oxidised to sulphur trioxide by air in the presence of platinum, but in this discovery he was preceded by Peregrine Phillips, a Bristol vinegar merchant, who in 1831 had already obtained an English patent for the manufacture of sulphuric acid: "In the said tubes I place fine platina wire or tubes of platina in any finely divided state, and I heat them to strong yellow heat...and I do affirm that sulphurous acid gas (SO_2) being made to pass with a sufficient quantity of atmospheric air through tubes as described...will be instantly converted into sulphuric acid gas, which will be rapidly absorbed as soon as it comes in contact with water (SO_3)^{9,54}.

Döbereiner claimed that platinum black "was not a simple but a mechanical combination of this metal with compressed oxygen gas, or in other words, that the platinum reduced or isolated by the wet method has the property of absorbing and then compressing a large amount of oxygen gas and that it becomes capable of combining chemically with diverse readily oxidisable substances. In the process of oxidation and acidification of alcohol, platinum plays a role corresponding to the function of the nitrous gases in the process of sulphuric acid formation"⁵³.

Thenard's work on the decomposition of hydrogen peroxide by metals and certain organic materials may be considered the origin of his interest in catalysis (without knowing the meaning of the phenomena). Thenard was astounded to see that the same material that decomposed water peroxide by simple contact was able to induce the reaction between oxygen and hydrogen. He understood that in order to comprehend the phenomenon he required the help of some one with a strong background in physics, and for this reason he requested the collaboration of Pierre-Louis Dulong (1785-1838). The results of this collaboration were described in two memoirs they published together^{55,56}. Thenard and Dulong found that other materials such as the sponges of palladium, rhodium, and iridium, presented the same characteristics as that of platinum. All these compounds lost this characteristic under conditions that Thenard and Dulong determined. In addition, compounds such as osmium, silver, charcoal, pumice stone, porcelain, glass, and rock glass acquired it at high temperatures.

In his study of the phenomenon of decomposition, Deville did also work in the field of catalysis. For

example, he found that when heating a mixture of potassium cyanide in contact with wet air, at 500 to 600°C, under vacuum, the pressure increased to about 1/2 atmosphere and maintained itself for many hours (potassium cyanide under the influence of water transformed into potassium formiate and ammonia). But if the potassium cyanide was first mixed with sponge platinum, large amounts of hydrogen were generated and a double cyanide of potassium and platinum formed. This hydrogen was not pure or accompanied by ammonia; it also contained 4 to 12 percent of carbon dioxide. Other results indicated that a concentrated solution of potassium cyanide at its boiling point attacked platinum. A lamella or sponge of platinum was transformed into a double cyanide of potassium or platinum and generated a volume of hydrogen proportional to the amount of platinum that dissolved. Mercury cyanide dissolved in water, did not attack platinum even at its boiling point. Nevertheless, addition of small amount of potassium cyanide resulted in the immediate separation of mercury that amalgamated with platinum⁵⁷.

Intensive research on the area of catalysis, particularly by Paul Sabatier (1854-1941; Nobel Prize In Chemistry, 1912) and others, led to the discovery that many metals, particularly nickel and the platinum group elements, possessed a unique catalytic activity that eventually would become the base of the fast development of the petrochemical industry. It was found that all platinum group metals, alone or supported, have strong catalytic activity, especially for hydrogenation reactions. Nowadays, they are used in reforming high-boiling fractions from the distillation crude oil at atmospheric pressure. The most important reactions are the dehydrogenation of alkylcyclohexanes, the isomerization and dehydrogenation of alkylcyclopentanes, and the dehydrogenation of cyclization of alkanes, all of which for aromatics, as well as hydrogenative cleavage of alkanes and naphthalenes, and dealkylation of alkylaromatics. The resulting product mixtures are gasolines with high antiknock properties. The most important catalysts are of the type Pt- γ - Al_2O_3 . The application of supported noble metal catalysts for the treatment of exhaust gases from automobiles has been introduced in recent years in all industrialized countries. Combinations of metals that have a catalytic action of exhaust gases include Pt-Rh, Pt-Pd, and Pt-Pd-Rh. The demand for these materials amounts to more than one-third of the annual

production of platinum and more than four-fifths of the annual production of rhodium.

Occurrence of platinum metals⁵⁸⁻⁶⁰

Platinum is a noble metal and shows considerable resistance to combine directly with many other elements. Accordingly, it is most commonly found in the uncombined state. The usual form of appearance is as an alloy known as native platinum. The metals and alloys of platinum are extremely resistant to weathering. The platinum mineral, usually called platinum ore, is usually composed of (a) sand formed by quartz, iron chromate and sometimes iron titanate, (b) an alloy formed mainly by osmium, rhodium and ruthenium, known as iridium osmiate or osmoiridium, that is insoluble in aqua regia and presents itself, normally, as small brilliant plates, rarely crystalline; as very small nuggets having a rough surface; or as lamella of graphitic look, (c) as an alloy of platinum, iridium rhodium, and palladium that forms the main part of the mineral, (d) copper and iron in the metallic state and, (e) gold and sometimes a little of silver. The content of platinum and metals varies between 45 to 86 percent. Platinum ores are concentrated in planetary regions, reaching near 30 ppm in the earth. All evidence indicates as to platinum being strongly siderophilic, fact that has led to considerable fractionation in the earth's interior, so that virtually the entire mass is in the earth's metallic core. This assumption is supported by the well-known presence of platinum in iron meteorites. The siliceous lithosphere is estimated to contain 0.05 to 0.5 ppm platinum. The platinum metal group metals in the lithosphere have been transferred from the earth's interior; tectonic movements of the earth's crust, followed by eruption of magma, have led to their presence in regions close to the surface. When primary deposits are altered and transported by the natural action of the hydrosphere and atmosphere, secondary deposits, also known as alluvial deposits, are formed. Mechanical concentration of the heavy constituents by flowing water takes place. Economically important deposits of platinum metals are preferentially connected with magmatic rocks rich in magnesia and low in silica.

Sources and production⁵⁸⁻⁶¹

Until the beginning of the nineteenth century, almost all platinum was obtained from Colombia, at the tune of about one ton per year. Afterwards, the mineral was also discovered in the Urals, California, Australia, Borneo,

etc., usually present in auriferous sands. A crude analysis of these sands indicates that in addition to copper and iron they contain about 12% of foreign matter, 80% of platinum and variable proportions of five rare metals, called platinum metals. Platinum and osmium form a compound that adheres to the steel mortars used trying to pulverize the mineral. This compound resists the action of aqua regia.

In 1825, Russia became the primary producer of platinum. The minting of platinum coins in Russia between 1828-1845 necessitated an increase in production, which reached 3.5 ton in 1843. Almost all of Russian platinum ore was used for coinage. The platinum industry grew vigorously after 1880 due to increasing demands for the electrical industry, dentistry, and chemical technology. In 1913, the annual production of crude platinum reached 7 ton. Platinum production was abandoned in Russia after the revolution, with the result that after World War I, Colombia once again became the largest platinum producer. In 1915, production in the Urals was restarted and new alluvial deposits were discovered in Siberia. For some decades, the Soviet Union was one of the largest producers of platinum, and especially palladium. By 1888, large deposits began to be discovered in South Africa, including the one known as the Merensky Reef, the largest in the world. After World War II, South Africa became the main producer of platinum. In 1911, the total world production of platinum was less than one ton, by 1950 total world production was 20 ton per year, in 1970—93 ton, in 1980—203 ton, and in 1990—222 ton⁵⁹.

Table 1—Platinum supply and demand (1000s oz)⁶¹

	2002	2003
Supply		
South Africa	4,450	4,670
Russia	980	1,050
North America	390	295
Others	150	225
Total Supply	5,970	6,240
Demand		
Auto catalysts: gross	2,590	3,190
recovery	(565)	(645)
Chemical		
Electrical		
Glass		
Petroleum		
Jewellery	2,820	2,440
Industrial	1,545	1,520
Investment	80	15
Total Demand	6,470	6,520

The great value of platinum metals for industrial use comes from its chemical inertness, high melting point, low vapour pressure, high temperature coefficient of electrical resistivity, low coefficient of thermal expansion, and exceptional catalytic properties, as explained before. All these properties have been exploited for industrial applications. Platinum, platinum alloys, and iridium are used for crucible materials for the growth of single crystals, especially oxides. The chemical industry uses a significant amount of either platinum or a platinum-rhodium alloy catalyst in the form of gauze to catalyze the partial oxidation of ammonia to give nitric oxide, which is the raw material for fertilizers, explosives, and nitric acid.

In recent decades, platinum has been in large demand for jewellery and high-quality watch making, particularly in Japan where platinum is preferred to gold. The use of supported platinum group metals for the treatment of exhaust gases from motor vehicles has been introduced in recent years in all industrialized countries. Regulations controlling the quality of exhaust gases can be complied with, only by the using such catalysts. In 2002, the automobile industry continued to be the major consumer of platinum group metals. Auto catalysts accounted for approximately 98 % of rhodium demand, 66% of palladium demand, and 41% of platinum demand. Another record year of platinum demand from the auto industry, is likely in 2004 due to further strong growth in European diesel car sales, as well as the increasing fitment of catalysed diesel particulate filters to light-duty vehicles in the region. During the first six months of 2004, diesel cars accounted for 46.8 percent of total new car sales in Europe, compared with just over 43 percent for the whole of 2003. An increasing number of new vehicle models already meet the Euro IV standards that will become effective in 2005. These will require substantial reductions in emissions of all major pollutants and in some cases auto manufacturers have increased platinum group metals loadings across catalyst systems in order to achieve them. In the diesel sector, platinum-catalysed diesel particulate filters are also being introduced on some larger, heavier car models to ensure compliance with tighter particulate matter emission limits. The use of platinum in gasoline vehicles is expected to account for almost 75% of demand from the European vehicle sector^{60,61}.

The use of platinum in electrical applications is also expected to rise, due to growing consumption of the metal in fuel cell development programs and increase in demand for high temperature thermocouples.

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