The Purity of Platinum

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Platinum as supplied to industry contains less than 200 parts per million of total impurities, and is probably the purest metal refined by chemical means alone. This article reviews the influence of individual impurities upon the properties of platinum, illustrates some of the sophisticated methods of analysis and control employed, and discusses the reasons why particular care is taken to eliminate specific impurities from platinum intended for use in certain applications.

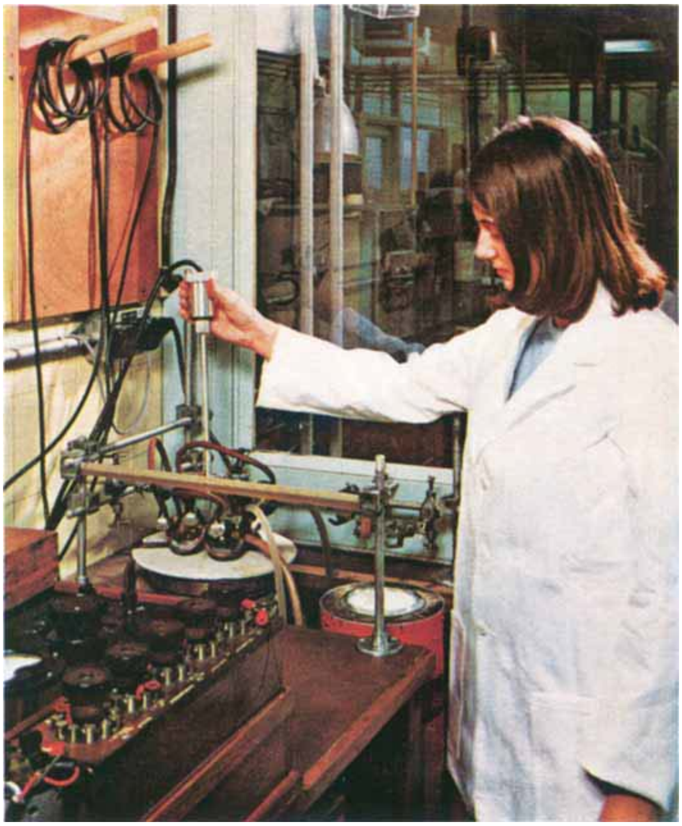
For nearly two centuries the platinum produced for treasuries, jewellers, scientists and industrialists has been among the purest of the World's metals. One of the reasons for this is severely practical. Certain of the naturally occurring impurities—and some of those introduced inadvertently in the processes first used for winning platinum—may cause the metal to shatter during hot-forging. The difficulties of Chabaneau in his secret laboratory in Madrid during the years when Spain enjoyed its brief Platinum Age are legendary—as when he was found throwing all his equipment and solutions out of the doors and windows in a fit of desperation—just three months before his successful production of a perfect 750 ounce ingot.

The temperamental behaviour of platinum in the early days cannot be attributed to the presence of any one impurity; iridium, iron, calcium sulphate, silicon (reduced from siliceous matter) have all been blamed and it is probable that all have given trouble at one time or another. Consistent production of malleable platinum was only established after Wollaston mastered the chemistry involved in precipitating a reasonably pure platinum salt.

Although there are no formally agreed purity specifications for commercially acceptable platinum, the general requirement that all metal must be malleable automatically ensures that the total of all impurities does not ever exceed 0.1 per cent, or 1000 p.p.m., and is usually appreciably less than a fifth of this.

An indirect specification for high purity, or at least freedom from certain deleterious, although unnamed, impurities has been in force for many years for platinum for use in resistance thermometers and thermocouples. This requires that the ratio of the electrical resistivities measured at 100 and 0°C shall be greater than a certain value (until 1968, 1.00358 and now, 1.003582). Nearly all of the common impurities in platinum depress the value, which is generally accepted as a sensitive indication of the overall purity of the metal. Another rapid and useful test, if the metal is available in the form of wire, is to couple it with a platinum wire known to be of high purity and to measure the e.m.f. developed between the cold free ends when the couple is heated to, usually, 1000°C. The presence in the wire under test of 10 p.p.m. by weight of iron alone, for instance, will be sufficient to produce an e.m.f. reading of about 15 microvolts; of silicon about 10 microvolts; and of iridium about 8 microvolts. The effects are additive. Although tests such as these are valuable, they give no precise indication of the influence of specific impurities; and this knowledge may be of considerable importance in developing new uses of platinum, new alloys and new structural forms.

One relatively simple assessment of the purity of platinum is provided by the sensitivity to impurities of its temperature coefficient of resistance. Nearly all of the common impurities depress the value, and by comparing the electrical resistivities at 100 and at 0°C an informative ratio is obtained. For use in temperature measurement, this ratio, R_{100}/R_0, must be greater than 1.003582



It is useful to think of the impurities in platinum as falling into at least seven groups: other platinum group metals, gold and silver, silicon, alkali metals, base metals, carbon and sulphur, and gases.

Platinum Metal Impurities

Small amounts of all five of the other platinum metals are almost always present in the purest platinum, and they can only be separated by repeated processes of chemical purification—mainly on the principle that by repeated partial precipitation of a platinum salt the impurities will in the end nearly all remain behind in the mother liquors. In such operations a stage is inevitably reached when a balance is struck and no further "purification" is achieved.

The following figures represent the probable amounts remaining in the purest platinum now available:

Ir	less than	1	p.p.m.
Rh	,,	1	,,
Pd	,,	2	,,
Ru	,,	2	,,
Os	,,	1	,,

The effects of low concentrations of these platinum metal impurities on the properties of platinum are not well established, but they do not seem to be significant, and there is no reason to believe that their combined effect is any different from the sum of the effects of each individually. No so-called synergistic reaction is involved.

In amounts of a few hundred parts per million, significant reduction in the temperature coefficient of resistivity is observed; and in rather larger amounts the platinum metal impurities may retard grain growth—particularly, it is thought, if some base metal impurities such as iron are also present. This property may be beneficial—particularly

Atomic absorption spectroscopy is used for the determination of other platinum group metals and of base metals in platinum being processed to check the efficiencies of the separation techniques. It is also used as a rapid check procedure against wet chemical analysis methods and emission spectroscopy

in laboratory ware such as dishes or crucibles, which may better keep their shape after repeated heating if they remain fine grain in structure.

Gold and Silver

In the purest platinum it is not difficult to reduce the content of gold and silver each to below 1 p.p.m.

Gold as an impurity has one unusual and quite unexpected effect. Like all other impurities it reduces the temperature coefficient of resistivity of pure platinum (100 p.p.m. by weight reduce it by about 0.07 per cent), but unlike any other it actually changes the sign of the thermoelectric power relative to pure platinum. Curiously enough, by the thermoelectric test, its presence thus makes platinum seem purer than it really is.

There is a school of thought which considers that traces of silver may be harmful to platinum under stress at high temperatures. It is suggested that, on account of the high vapour pressure of silver—about 15,000 times that of PtO_2 at 1500°—there may be selective evaporation of silver, leaving vacancies which may come together and form nuclei for cracks. It is difficult, however, to find experimental evidence to support this view. There is certainly a body of experience to associate cracking of platinum in service at high temperatures—and of welds in platinum—with traces of silver, but there is an even more voluminous evidence from controlled high temperature tests that a few hundred parts of silver may not only be tolerated but may sometimes be beneficial. It is possible that only in certain restricted ranges of temperature and stress that vacancies can form and come together by the mechanism outlined.

Silicon

In quite small concentrations, above about perhaps 0.1 per cent, silicon is well known to form the platinum-platinum silicide eutectic, which concentrates as a lowmelting film around the grain boundaries and causes disastrous cracking when the metal is heated above about 900°C. But it is only recently that it has come to be realised that in much smaller amounts silicon is one of the most damaging to the electrical properties of all the impurities which are commonly found in platinum. The presence of 1 p.p.m. by weight of silicon, for instance, has as damaging an effect on temperature coefficient as 10 p.p.m. of gold.

Silicon, moreover, can be present in platinum in two forms—either in solid solution or as inclusions of silica derived either from refractories or even—as very small particles—persisting from silica contamination (derived from vessels, water or chemicals used in its production

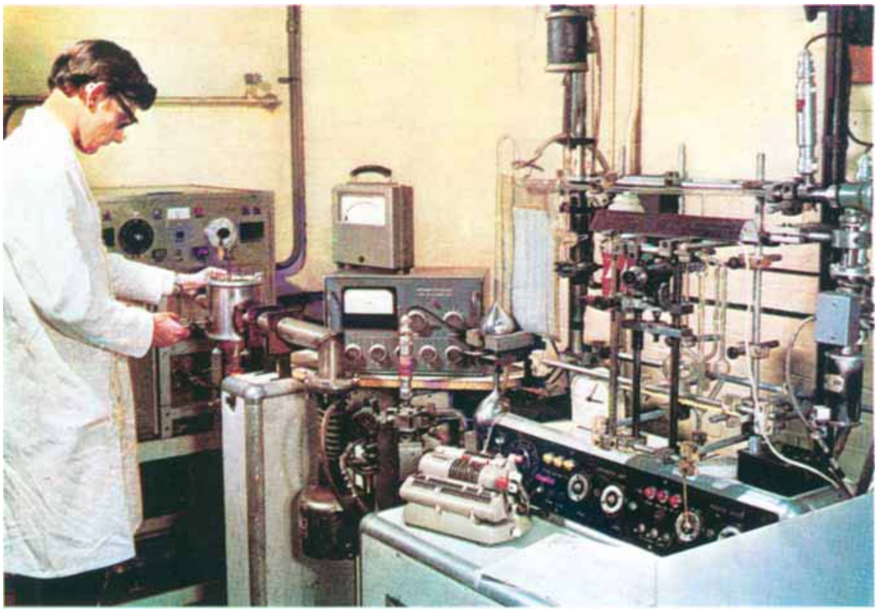
Silica contamination may be expected to be more prevalent in powder metallurgy platinum than melted platinum; and more frequent in platinum melted in air in oxide refractories than in platinum melted in metal boats in vacuum—since in the latter material there is every opportunity for the silica to be reduced to silicon.

Silica inclusions are difficult to detect and fortunately small amounts generally seem to do little damage. They may, however, be the source of some of the gas which is evolved when a bar of platinum is subject to vertical zone refining in vacuum. The action, which has been recorded by numerous experimenters, is often violent and not easily explained. It seems likely, however, that in these conditions the silica will be reduced in the molten zone either by reaction with traces of carbon or simply by molten platinum itself, a process which will proceed rapidly as the evolved oxygen is pumped off.

Alkali Metals

Traces of calcium, sodium and potassium might well be expected in platinum, residues from the long series of chemical processes always involved in its refinement. Calcium

This modern direct reading spectrograph can detect impurity levels for many elements down to less than 1 part per million and can record these levels for 42 elements in a single operation



The determination of oxygen, hydrogen and nitrogen is carried out in the vacuum fusion apparatus. More complete information on the gas content of platinum is obtained in similar equipment where the conventional low pressure gas analyser shown here is replaced by a mass spectrograph

was always to be found in platinum which had been melted on a lime hearth, and was thought to be effective in reducing grain size—probably through the formation of insoluble calcium compounds with other trace elements and their action in restraining grain growth.

Traces of sodium and potassium chlorides may also be found in powder metallurgy platinum, and in the early days of platinum thermometry their presence was thought responsible for "sparking" observed when wires of this product were melted in a blow-torch. In modern platinum, melted in zirconia or zircon refractories, alkali metals are seldom detected and it seems unlikely that their content exceeds 1 p.p.m.

Base Metals

Iron is the most troublesome of all base metals in platinum. Hot platinum very readily alloys with any iron with which it is in contact, and the iron diffuses rapidly below the surface. Thus the operations of hot forging or hot rolling always contaminate a platinum ingot, and in making pure platinum it is essential to scalp all material after hot working operations. Even cold working can introduce iron as an impurity. Any scuffing or rubbing may transfer a smear of iron to the platinum surface, and it is essential to remove this (by some means such as chemical etching) before the platinum is annealed, otherwise the iron may diffuse deeply into the mass.

Iron and chromium (which, luckily, is a less persistent impurity in platinum) come next after silicon in their damaging effects on the temperature coefficient of resistivity of platinum, and thus special care is necessary in producing Thermopure platinum to keep iron contamination to a minimum.

Of the other metals, aluminium has been blamed for intercrystalline brittleness and poor welding quality, as have lead, zinc and tin; but the amounts needed to cause such damage are well in excess of 10 to 100 p.p.m.; in modern high purity platinum none of these metals is present to a greater extent than 1 to

2 p.p.m. The presence of up to about 5 p.p.m. of copper is not unusual, but there is no evidence that this is in any way objectionable.

Carbon and Sulphur

Recently, Darling and his colleagues have shown that small quantities of carbon can be held in platinum in solid solution, and it seems reasonable to believe that a few parts per million of this element may be present in all platinum.

Similarly, a trace of sulphur would not be unexpected.

Oxygen and Hydrogen

It seems as certain as any dogmatic statement concerning platinum can be that oxygen and hydrogen are without any measurable or detectable solubility in pure platinum. Platinum bulbs can be used for a gas thermometer for the most precise fundamental measurements without the slightest fear that oxygen or hydrogen will pass in either direction or influence the most precise determinations.

For hydrogen, this viewpoint has never been questioned. But for oxygen, observations of internal oxidation in alloys of platinum with quite small amounts of such easily oxidisable metals as chromium have suggested that oxygen atoms can diffuse through the platinum lattice.

The fact, however, that internal oxidation is observed in alloys of platinum does not necessarily imply that the oxygen penetrates through pure platinum. It seems equally likely that in these materials it is the atoms of the alloying metal, possibly concentrated at the grain boundaries, that combine with the oxygen atoms, handing them on so to speak from one to the other through the strained platinum lattice. In the absence of these oxidisable alloying metals, oxygen may well be quite unable to diffuse through platinum.

Commercial Production of Pure Platinum

It will be apparent that this review has attempted to rationalise the traditional aim of platinum refiners for high purity. Some

X-ray fluorescence spectroscopy is used extensively to determine many of the elements in platinum to be refined and for monitoring some stages of the refining operations. This instrument is controlled by a novel logic unit enabling up to 25 elements to be determined automatically. The X-ray data is processed in a central computer impurities may unquestionably be tolerable generally; some, although tolerable for most purposes, must be strictly controlled for specific applications; and some are nearly always damaging.

There is thus ample justification for the policy of producing a grade of platinum from which all the generally damaging impurities are carefully excluded and which has been purified as far as is commercially prudent from all others.

Modern production methods rely for this purpose on regular monitoring for specified impurities throughout the refining process. Routine chemical and physical tests have, of course, always been used—as well as the eyes of the operators—to spot at once any tell-tale change in the colour or texture of intermediate precipitates. Spectroscopy was brought into service many years ago, and as the techniques of arc emission spectroscopy have been developed so they have been applied for the detection and estimation of impurities in platinum refinery products. The limit of detection for most elements is now about 1 p.p.m.; although unfortunately amounts of less than 10 p.p.m. of iridium, and 10 p.p.m. of ruthenium may still pass undetected in routine methods of testing. However by special more time-consuming techniques, the limits for all these elements can be reduced considerably.

In addition to improvements in reliability and sensitivity, the introduction of direct reading instruments and data processing facilities have been accompanied with obvious savings in time and skilled man-power and have encouraged the greater use of the method.

For some products X-ray fluorescence spectroscopy has also found a place, also now with a high degree of automation. Gas analysis has yet to be pressed into service for routine control purposes, though it is of value for research and investigational projects. Finally radiation checks are regularly carried out to ensure the absence of contamination by any radioactive species—such as traces of uranium.

All this means that corrective tests to eliminate unexpected contamination and unwanted impurities are now taken early in the refining process, so that it is no longer necessary to wait for the final stages to test for purity by measuring such properties as malleability and temperature coefficients of electrical resistivity.

It is also possible to grade platinum as it comes from the refinery into standard grades, to select purer batches as required, and in special instances to earmark batches for specific purposes.

The bulk of the metal produced is marketed as "Commercial Platinum". This seldom contains more than a total of 200 p.p.m. of impurities and is internationally accepted as of good marketable quality. Slightly purer grades with a maximum of 100 p.p.m. of impurities are also available and are preferred particularly for fabricated forms which are to be used at high temperature.

For thermocouples, "Thermopure" platinum containing less than about 20 p.p.m. of total impurity is selected to meet the requirement of low e.m.f. at 1000°C when coupled to a pure platinum standard. For resistance thermometry, platinum is supplied to meet specified requirements for temperature coefficient of electrical resistance.

Finally a high purity or "Specpure" grade of platinum is available containing a total of less than 5 p.p.m. of detected metallic impurities.

It is of some interest that these grades of platinum are all produced by chemical means, so that platinum is probably the purest metal to be refined by chemical means alone.

Further refining by physical means, as by zone refining in oxygen or by distilling off impurities at high temperature in oxygen or in vacuum might possibly reduce some of the residuals discussed in this article to still lower figures. With our present knowledge it would seem, however, that the resulting pure platinum would be undistinguishable from the present product in any of its physical, mechanical, or chemical characteristics.