

# Platinum Metals in the Development of Analytical Chemistry

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The Science Museum, London

The celebration of the centenary of the foundation of the Society for Analytical Chemistry is an occasion for looking at many features of the history of analytical chemistry. Platinum and, to a lesser extent, the other platinum metals have played a distinctive part in the progress of this branch of science.

A glance at a few of the familiar characteristics of platinum show why it has been important. It is unreactive, which makes it an excellent vehicle for use in contact with a variety of reagents. It has a high melting point, which makes it an excellent vehicle for high temperature reactions. Its electrochemical properties make it an almost unique material for electrode systems.

Against it could at first be set the difficulty of working it, a much greater obstacle than expense (it was comparatively cheap for a long time). The first platinum crucible ever to be made was almost certainly the one described in 1784 by Professor Franz Achard of the Royal Academy of Sciences in Berlin. By using the old arsenic process of rendering

platinum fusible and a clay mould and former he succeeded in making a crucible "which is hammered a little on a mandrel and is then ready". This must have been a very fragile article, and there is no further record of Achard's crucibles.

Guyton de Morveau records in 1786 that:

"I have platinum crucibles which have been very useful in a number of researches, as for example for the decomposition of minerals according to Bergman's method."

A year later Guyton de Morveau, referring to the increasing availability of platinum, expressed the hope that "we shall soon be able to make vessels and other apparatus". But according to Kopp's History of Chemistry platinum apparatus remained a rarity for chemists at the turn of the eighteenth century.

## Torbern Olaf Bergman 1735-1784

*Professor of Chemistry at the University of Uppsala, Bergman laid the foundation of quantitative analysis. He introduced the systematic use of reagents and the concept of determining metals in the form of their insoluble compounds*



## Centenary of the Society for Analytical Chemistry

*The Society of Public Analysts, founded in 1874 as a means of exchanging information on methods of analysis, is celebrating its centenary under its modified title of the Society for Analytical Chemistry. The contributions to analytical techniques made by the platinum metals both before and during the hundred years of existence of the Society are reviewed here.*



The history of the perfecting of the method of fabricating platinum at the hands of W. H. Wollaston and others has often been told. Wollaston was the first to use it to make laboratory vessels on any scale, beginning in 1805. Its unreactive nature was now fully appreciated, and by Wollaston's day the techniques of analysis had been brought to a respectable degree of systematic discipline, as regards theories of composition. The practice had also been refined to such an extent that analysts like Kirwan, working on siliceous minerals, were able to make quantitative estimates of the interference with their results of material derived mechanically or chemically from the glass or earthenware vessels in which their reactions were carried out. The campaign for constancy of conditions and purity of reagents which was led by analysts like Vauquelin was one which benefited from the constancy and unreactivity of platinum as a material for the construction of crucibles.

The introduction of the platinum crucible for routine use in gravimetric analysis did, however, take time. Apparently there was only one in Sweden in 1808, made for (or by) the foundry-owner Hisinger, who aided and befriended Berzelius. Hisinger lent this to Berzelius, but it was of some size and too heavy for use on the balance that Berzelius

was using at that time. However, in 1823 when Wöhler arrived to study with Berzelius he was given a platinum crucible for his own use. Wöhler was Berzelius' only student for some time, so there may not have been many about, but at least there was one to spare.

Berzelius' Text-book of Chemistry, that monumental summary of the chemical theory and techniques of the third decade of the nineteenth century, tells us a good deal about the use of the platinum crucible. Ignitions and fusions had formerly been carried out in clay crucibles which, while well established for metallurgical work, were proving unsatisfactory for much of the more refined chemical work now being done. Platinum thus superseded clay as a favoured crucible medium. Berzelius warned against a number of dangers; for example, metals could not be fused in platinum because of alloy formation which embrittled or destroyed the platinum, and aqua regia, of course, could not be heated in it. Less expected was what was described as the dire effect of a sooty flame, which appeared also to produce embrittlement. (That this is due to carbon but to the simultaneous effect of undesirable substances being fused was not cleared up until much later. A possible explanation is that some of the low melting point fluxes used, over a low temperature flame, were inimical to the

platinum, so the sooty flame was blamed for the faults of fluxes.)

The familiar porcelain crucible was only just coming into use at this time. Although porcelain manufacture for decorative purposes had been perfected early in the previous century, only in the 1820s were porcelain crucibles made which would stand even moderate heating. At first one important use for a platinum crucible was as a shield and support for one made of porcelain.

By the time that the Society of Public Analysts was formed platinum ware had, of course, become essential and commonplace. A writer in "The Chemist and Druggist's Diary" of that very year comments:

"Next in importance to the balance, utensils of platinum must be considered. Of these are required at least one crucible of about an ounce capacity, costing 30s; a capsule holding rather over 100 cc for water residues, a bundle of wire, and if nickel and copper analyses are to be made a platinum knife should be added."

The rapid development of experimental techniques in the late nineteenth century made it possible for the properties of platinum to be more closely studied than before, with some loss of its reputation as a virtually impregnable material, and some greater understanding of the conditions under which it could behave at its best. No-one has kept, so long after his death, so high a reputation for experimental skill as William Crookes. Towards the end of his career, in 1908, Crookes published several studies of the

properties of the platinum metals. He asserted the virtues of iridium as a material for the construction of crucibles, and one of those made for him by Johnson Matthey survives to this day. In recent years iridium has been used for melting special glasses and for growing the synthetic materials for laser optics.

## Electrolytic Methods

The processes of gravimetric analysis were rendered intelligible and self-consistent by the introduction of Dalton's atomic theory with its universal arithmetic basis. It required the quantitative laws of Faraday to make electrolysis into a useful analytical method. The qualitative distinction between electropositive and electronegative elements was made quite early after the discoveries of Volta, and Nicholson and Carlisle, and became the basis of important theories of chemical constitution. A link with the qualitative theories of composition was made by the discovery by Faraday that, when metals were deposited at a cathode or a gas

### Jöns Jacob Berzelius 1779-1848

*Among his many great contributions to chemistry, Berzelius carried out analyses of many rare minerals and improved analytical methods. He discovered cerium, selenium and thorium, and also standardised the methods of separating the constituents of native platinum on an analytical scale*





### Wolcott Gibbs

1822-1908

*Born in New York, Gibbs graduated at Columbia and then studied in Germany under Liebig and in Paris under Dumas and Regnault. In 1849 he became Professor at what is now the City University of New York, later accepting a chair at Harvard. His researches were mainly in analytical chemistry; among other achievements, in 1864 he was the first to introduce quantitative electrochemical analysis*

was liberated at an anode, the quantities liberated were related both to the equivalent weights and to the quantity of electricity passed. This could have been, from the outset, the basis of a system of electrolytic or electrogravimetric analysis, but this in fact had to wait until the work of Wolcott Gibbs in 1864.

His apparatus, although simple and soon superseded, set the pattern for most work to follow. The electrolyte was contained in a platinum crucible acting as cathode, the anode being a central platinum wire immersed in the electrolyte. He determined copper and nickel by deposition on the weighed cathode but this was not a coulometric method, the current being used solely to effect complete decomposition of the electrolyte. Its logical form was the same as that of traditional dry assay (total extraction of the desired species from a weighed sample), but the factors interfering with rapidity and completion provoked a number of developments in the physical form of the cell used.

Platinum remained the essential material but electrodes became more involved in shape as more was learned about the physical

behaviour of deposits and about the basic electrochemistry.

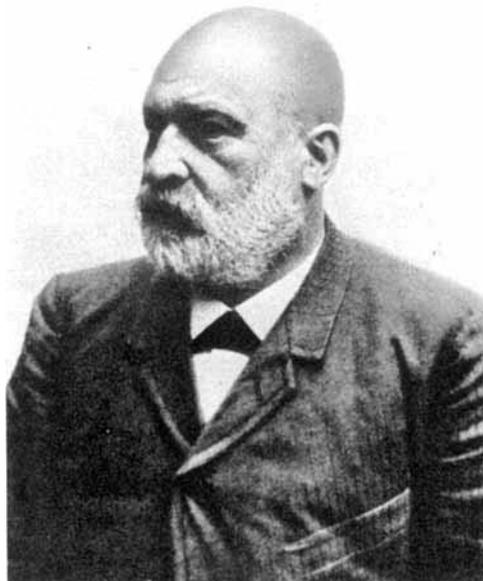
One of the earliest workers in the field, acting independently of Wolcott Gibbs, was C. Luckow. In 1895 he reviewed the early progress of electrochemical methods and described his own electrodes, a platinum cylinder as cathode with a horizontally mounted platinum disc having a vertical wire stem from its centre. He also introduced the flat spiral anode. He also claimed to have been determining copper and silver by electrolysis in 1860, before Gibbs, and certainly he was responsible for introducing this technique into industrial laboratories.

It was appreciated early on that current density at different points on the surface of the cathode could have a profound effect not only on the amount of deposition at any point but also on the structure of the deposit. Clemens Winkler, Professor at the Freiberg School of Mines, was one of those who devised novel forms of electrode systems and he was the first to employ a platinum gauze cathode with its advantages in circulation of the electrolyte.

More effective in the releasing of gases was the rotating anode, like that described at the first meeting of the Faraday Society in 1903 by F. Mollwo Perkin. He suggested another improvement, the use of an alloy of iridium and platinum in place of platinum. Perkin

**Clemens Alexander Winkler**  
**1838–1904**

*Professor of Chemistry at the Freiberg School of Mines, Winkler was an outstanding inorganic chemist of his time. Among his achievements was the discovery of germanium, and in 1899 he proposed the use of the cylindrical cathode made of platinum gauze, still in use today, for electrochemical analysis*



pointed out that although platinum was usually regarded as a metal practically unaffected by any reagent other than aqua regia, it was by no means as resistant as had been thought under some conditions of electrolysis, particularly in the presence of cyanides. Iridium or a platinum-iridium alloy was more resistant, and its use was taken up. Iridium presented great difficulties in working, and Perkin recommended that chemists should not attempt to prepare their own electrodes but should get Johnson Matthey to do it for them.

So far this brief note has dealt only with electrogravimetric methods. Another branch of electrochemistry also developed in the late 19th century. Hydrogen ion concentration has a special place in the theory of electrolytic dissociation, and the measurement of pH is perhaps the most frequently performed electrochemical procedure. Platinum played its part in the development of the theory of hydrogen ion concentration, and thus in the development of analytical techniques. In 1893 Le Blanc found that if a stream of hydrogen is allowed to flow over the surface of a platinum electrode this behaves as a hydrogen electrode, i.e. if immersed in a solution of an acid it behaves like a metal electrode immersed in a solution of that metal ion. The studies of hydrogen ion concentration made possible by this electrode system led to the theory of indicators, to the concept of buffer solutions, and to the pH concept developed by Sørensen and others in their study of enzymes.

The recognition of platinum as a distinct element was slow and uncertain, the metal having been found and used long before the modern concept of chemical purity emerged in the early nineteenth century. Ideas of purity and methods of analysis did in fact develop hand in hand. Wollaston's separation of the other platinum metals from platinum itself by treatment of crude platinum with aqua regia followed by mercuric cyanide was not an isolated experiment. The stepwise separation of complex mixtures had been initiated by Bergman and in the hands of Kirwan and Klaproth was already very similar to the systems of group separation which were to become the backbone of inorganic analytical chemistry for a century or more. The platinum metals separation is a distinctive example of the discipline of analytical procedure which was to reach its peak in the rare earth separations of William Crookes.

No doubt the history of analytical chemistry could be written without specific mention of platinum and its allied metals but such a history would fail to do justice to an interesting and, in many respects, vital contribution.