

Raleigh Gilchrist and His Research on the Platinum Metals

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Raleigh Gilchrist, one of America's most prominent internationally known authorities on the chemistry of platinum and of gold, was born in the small town of Windsor, Vermont on January 8th, 1893, but moved with his family to Great Falls, Montana in 1896. It was here in 1910 that Gilchrist first became involved with noble metals when, in order to earn money to enable him to attend college, he began work as an assistant for the Anaconda Copper Mining Company handling gold and silver slimes.

In September 1911 he entered the University of Montana at Missoula, from which he received his B.A. degree with a major in chemistry in 1915. He then began graduate study in inorganic chemistry at Cornell University with an assistantship in qualitative analysis. Later, in November 1917, when he had begun his doctoral research on germanium compounds he was inducted into the U.S. Army. Soon he was transferred to the Inorganic Chemistry Section of the National Bureau of Standards in Washington where, under Dr. William Francis Hillebrand, he was required "to engage upon a program of investigation of the refining and analytical chemistry of the platinum group metals". It was during a successful career of 45 years at the Bureau, briefly at first as a soldier and later as a civilian, that Gilchrist carried out the work for which he is remembered.

In order to resume his graduate work while still remaining at the Bureau, Gilchrist enrolled at the Johns Hopkins University in Baltimore, where he began a new doctoral research problem under Dr. Joseph Christie Whitney Frazer with minors in physical chemistry and physics. He was not required

to take any class work, but he audited a course in colloid chemistry from Dr. Walter A. Patrick, who played an important role in the commercial production of silica gel. Gilchrist received his doctorate in 1922 with a dissertation "The Preparation of Pure Osmium and the Atomic Weight of Osmium", which was published in 1922 under the title "A New Determination of the Atomic Weight of Osmium" (1).

At the National Bureau of Standards Raleigh Gilchrist rose through the ranks to become Chemist in 1936, and later Chief of



Raleigh Gilchrist
1893-1966

An internationally recognised authority on the analytical chemistry of the platinum metals, the subject to which he devoted 45 years of work at the U.S. National Bureau of Standards

Photograph by courtesy of Mrs. Elizabeth R. Gilchrist

the Platinum Metals and Pure Substances Section of the Division of Chemistry. From 1948 to 1961 he was Chief of the Inorganic Chemistry Section. He retired in November 1962, after which he served as consultant to the Chief of the Chemistry Division. His duties initially consisted of planning and carrying out experimental chemical research on methods for preparing each of the six platinum metals in pure form and of developing a knowledge of their chemistry. In addition he tested for chemical composition a variety of noble metal alloys, materials, and articles from other governmental agencies, and he analysed materials where disputes had arisen between commercial chemists. He developed methods for analysing materials containing the platinum metals, gold, silver, and the base metals usually associated with them. In his later years he also worked on the purification of sulphur, nickel, zirconium, barium, strontium, germanium, and the rare earths as well as on the preparation of titanium halides and the analysis of ceramic dielectrics. The results of his systematic studies were of great practical value and have been utilised by the noble metals industry, displacing older, inadequate procedures, and by scientists in the aeronautical, dental, and industrial fields. He also supervised the preparation of pure substances and the testing of reagent chemicals.

Gilchrist travelled widely, both on official business and for pleasure, his first trip to Europe in 1926 being "to establish friendly relations with foreign laboratories in which research on the platinum metals was being done, to become acquainted with professors working on these metals and to see as much of the great platinum works as possible and to discuss problems of mutual interest" (2). Not surprisingly his first call was at the offices of Johnson Matthey and Company at Hatton Garden in London.

In 1936, 1938, and 1948 Gilchrist was a member of the United States Assay Commission, which meets yearly at the U.S. Mint in Philadelphia to check coinage. He was an

official United States delegate to a number of international conferences, including, in 1934, the Third International Technical and Chemical Congress in the Agricultural Industries (Paris), the Eleventh Conference of the International Union of Chemistry (Madrid), and the Ninth International Congress of Pure and Applied Chemistry (Madrid). At the last-mentioned meeting, he presented the paper for which he was awarded the Hillebrand Prize four years later (3). In 1927-1928 and 1929-1934 he was a lecturer in chemistry (thermodynamics and advanced inorganic) at George Washington University and in 1928-1929, 1931-1932 and later years a lecturer in chemistry at the National Bureau of Standards Educational Schools.

Throughout his working career Dr. Gilchrist undertook an active part in the work of many honorary, scientific and fraternal organisations. For almost half a century he was a member of the American Chemical Society and held continuous office in the Chemical Society of Washington for 32 years, being Secretary in 1925 to 1928 and President in 1929.

A perfectionist both in his work and in his avocations, Raleigh Gilchrist died in Washington on October 26th, 1966 at the age of seventy-three.

Gilchrist's Work

During World War I when the U.S. supply of Chilean saltpetre from the Atacama Desert was threatened by German submarines it became necessary to produce synthetically the nitric acid and nitrates needed for explosives. Because of the resulting intense interest in nitrogen fixation, Dr. William F. Hillebrand's dream of creating a laboratory to refine the platinum metals and to develop methods for determining the individual metals became a reality. Young Gilchrist was assigned to work on the analysis of iridium-platinum gauzes used to convert ammonia to oxides of nitrogen and eventually to nitric acid by the process invented by Ostwald in 1901. The assignment was soon widened in

scope, and in the course of years analyses at N.B.S. under Gilchrist's supervision were made on "a wide variety of materials, ranging from the determination of the quantity and thickness of the gold wash on the inside of a cocktail goblet to that of the composition of the highly complex native grain platinum" (4). The preparation of the platinum metals in highly pure form for the determination of various physical properties such as atomic weight required additional treatment of the commercial metals, and this task was also within Gilchrist's purview.

Gilchrist found that most of the analytical methods in the literature for the platinum metals did not produce clean-cut separations, particularly the venerable precipitation of platinum with ammonium chloride and the extraction of metallic mixtures with acids or with molten pyrosulphate. One remarkable exception was the insolubility of iridium in molten lead, employed by Deville and Stas in analysing the iridium-platinum alloy used in fabricating the international prototype metre and kilogram (5). In this method the alloy is melted with ten times its weight of lead, producing alloys of lead and platinum, which are soluble in acids, and crystalline iridium, which is virtually insoluble in aqua regia. In his first publications (6, 7) Gilchrist confirmed the accuracy of the method and modified it to increase its ease and speed of operation. The method is an excellent one for the routine analysis of platinum alloys containing no iron, ruthenium or osmium. Beamish (8) recommends it for determining iridium in platinum or palladium alloys, in which the latter two noble metals are not to be determined. The method is readily adaptable to massive forms of alloys such as sheet or wire.

Weeks (9) has called ruthenium "the little Benjamin of the platinum family" because it saw the light of day so much later than its older brothers. Gilchrist devised a gravimetric method for this least known member of the platinum metals group that involved the principle of controlled hydrolytic precipitation (10), a principle employed in crude form

as early as 1835 by Döbereiner, who used lime water to isolate platinum from osmium, rhodium, iridium, palladium and copper (11). Gilchrist added enough NaHCO_3 to the solution to turn bromocresol indicator faintly purple, and he then boiled and filtered the solution. The precipitate is ignited in a hydrogen atmosphere and weighed as metallic ruthenium.

Although distillation of OsO_4 , usually from a solution acidified with nitric acid, has been generally used to separate osmium from the other platinum metals, no study of the optimum conditions or completeness of separation was made until Gilchrist's study of 1931 (12). He found that the form in which the osmium exists in solution has a marked effect on the rate at which it is volatilised. He used a 6 N hydrochloric acid solution saturated with sulphur dioxide for absorbing the distilled OsO_4 , and the osmium was recovered from this by hydrolytic precipitation with NaHCO_3 . The hydrated OsO_2 was ignited in hydrogen and carbon dioxide and weighed as metallic osmium. Gilchrist concluded that a complete separation of osmium from the other platinum metals is possible by the traditional method if proper precautions are observed. More recent investigations (13, 14) resulting in low values by use of Gilchrist's SO_2 -HCl receiving solution have been shown to be due to ageing of the solution rather than to actual loss of osmium (15).

During the period 1915 to 1943 only two chemical determinations of atomic weights of the platinum metals were made—osmium by Gilchrist (1) and ruthenium by Gleu and Rehm (16). From the osmium content of $(\text{NH}_4)_2\text{OsCl}_6$ and $(\text{NH}_4)_2\text{OsBr}_6$, Gilchrist, returning to the topic of his doctoral dissertation, proposed the value 191.5, one considerably below today's accepted value of 192.2, obtained from isotopic abundance ratios (17).

Gilchrist's work, however, was not limited to research on the individual platinum metals but encompassed the separation and determination of each of the metals in the presence

of the others. An important step in this direction was his paper on "Purification of the Six Platinum Metals", published in 1928 (18). In 1923 Wada and Nakazono noted that rhodium is precipitated by the reducing action of $Ti_2(SO_4)_3$, while iridium is not if the chloride solution of each metal is treated separately (19). Gilchrist developed this qualitative observation of selective reduction into a quantitative separation of the two metals and their gravimetric determination (20). The rhodium is redissolved in boiling sulphuric acid, reprecipitated by hydrogen sulphide, ignited in hydrogen, and weighed as metal. The titanium, now in the tetravalent state, is precipitated from the filtrate with cupferron ($C_6H_5N(NO)ONH_4$). The iridium is precipitated from the filtrate hydrolytically with $NaHCO_3$, and the $IrO_3 \cdot nH_2O$ is ignited in hydrogen and weighed as metal. The recent chromatographic method of Rees-Evans et al. (21), modified by Payne (22), has been reported to be simpler than Gilchrist's titanium method.

In 1934 Gilchrist devised a procedure for the separation of ruthenium from platinum, palladium, rhodium and iridium based on hydrolytic precipitation (23). In the same year he employed hydrolytic precipitation by $NaHCO_3$ (pH 6) in the presence of $NaBrO_3$ (which prevents hydrolysis of $PtCl_6^{2-}$) to remove palladium, rhodium and iridium from a solution containing platinum (24). The platinum remaining in solution is precipitated by hydrogen sulphide, dissolved in aqua regia, precipitated with sodium formate, ignited, and weighed. Palladium is precipitated with dimethylglyoxime (25), ignited, and weighed as metal, while rhodium and iridium are determined gravimetrically by Gilchrist's earlier procedure (20).

By 1934 Gilchrist and his colleague Edward Wichers had developed a new and reliable procedure for the separation and gravimetric determination of all six platinum metals based largely on Gilchrist's work of the previous decade cited above. The method, which was simpler than the methods previously used,

was discussed in the paper "A New System of Analytical Chemistry for the Platinum Metals" (3), presented by Gilchrist at the Ninth International Congress of Pure and Applied Chemistry, for which he and Wichers received the Hillebrand Prize (26). Osmium and ruthenium are first removed by distillation, and palladium, rhodium and iridium are separated from platinum by a hydrolytic precipitation with $NaHCO_3$ under conditions of controlled acidity (pH 6 to 8) that leaves platinum, whose chloride complex undergoes no appreciable hydrolysis, alone in solution. The detailed analytical procedure appeared in the *Journal of the American Chemical Society* (27) and has been experimentally re-evaluated (28; 29, p. 67). It should be noted that researchers comparing hydrolytic methods with other methods are in effect examining their ability to use the method, which requires considerable experience and skill, especially with small samples (29, p. 75). Gilchrist also authored a number of review articles on the platinum metals in books, encyclopaedias, and journals (30-35).

Conclusion

At the beginning of Gilchrist's career, the state of development of the analytical chemistry of the platinum metals lagged far behind that of the other groups of metals, the methods then used being incomplete, inefficient, inaccurate, and inconvenient. Although in a number of cases, the methods developed by Gilchrist have been superseded by more modern methods, the fact that today the separation of the platinum metals is no longer shrouded in mystery is due in no small part to his pioneering efforts. Thanks to Raleigh Gilchrist and those who followed him, reliable procedures based on simple reactions are now available for the analysis of platiniferous materials—procedures comparable in accuracy with the best in use for more common metals.

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Platinum Process for Photographic Prints

A nearly forgotten photographic process which produces platinum prints with a most attractive appearance and a permanency which far exceeds those produced by more conventional processes is recalled in a recent article by G. L. Wakefield (*Amat. Photogr.*, 1976, **154**, (25), 67–69). Processes employing platinum group metals have been known for over a hundred years and as early as 1873 William Willis was granted a patent for "Improvements in Photo-chemical Printing" where he employed salts of platinum and iridium. In more recent times commercial availability of the sensitised materials has

been progressively reduced and at the same time the development of newer techniques has displaced the necessary processing data from many of the photographic textbooks.

Prints of considerable age produced by one or other of these platinum processes can still be seen in many of the larger collections of photographic prints where their intrinsic beauty can be admired and the technical skills of the photographer appreciated. Although unlikely to have much influence on the present photographic situation the techniques still appear to offer considerable potential to the creative enthusiast.