PLATINUM ORE ANALYSIS.

BY

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Analysis of Platinum Ores.

Crude platinum has, for a long time, greatly interested the analytic chemist. Nevertheless, it was not until, in the present century, the discovery of the metals, iridium, rhodium, osmium, ruthenium, and palladium, was made, that anything like a complete method of analysis could be suggested. And, even in the light of our present knowledge, the analysis of crude platinum is a tedious and unsatisfactory process. The difficulties of complete and accurate separation of the metals of the platinum group are great, and the chances of loss many. It is not surprising, then, that the methods proposed are intricate and long; nor is it reasonable to hope that they will be greatly improved in these regards. I realized all this when I agreed to undertake the analysis of a number of samples of platinum ore, kindly furnished me by Mr. Geo. F. Kunz, of Tiffany & Co., New York. My object was to devise a method as simple and expeditious as was consistent with accuracy and applicable to very small portions of the ore. The latter feature was necessarily introduced because of the very small samples furnished; no one of which afforded more than one and a half grammes and several much less than one gramme. The material obtainable for preliminary experimentation was likewise very limited and had to be very carefully husbanded. The method determined on and subsequently used is given in another part of this paper. I wish first to give a very brief epitome of the more important methods which have been already proposed for the quantitative analysis of these ores. The first of anything like completeness was one reported by Berzelius in 1828, the next was by Claus in 1854, and the last, especially adapted to quantitative analysis, by Deville and Debray in 1859.

Method of Berzelius.

The ore is first mechanically freed from foreign matter and then, in a retort connected with a cooled receiver, is heated with hydrochloric acid and successively added portions of nitric acid until the residue becomes syrupy. This is then leached with water and the insoluble portion retreated as often as necessary. The distillate is neutralized with ammonia or lime and the osmium precipitated by hydrogen sulphide. The water solution and the residue are boiled until the odor of chlorine disappears and then filtered. The insoluble portion is iridosmine. The filtrate is mixed with alcohol and a saturated solution of chloride of potassium. The resulting precipitate is washed with dilute alcohol and sal-ammoniac. The double chlorides of platinum, iridium and rhodium remain. They are carefully heated with sodium carbonate. The platinum is reduced to the metalic state, iridium and rhodium remain as oxides. The mass is washed free from alkali and then ignited and weighed. It is fused with bisulphate of potassium as long as rhodium can be leached out with water. The most of the platinum is removed by dilute aqua regia; the remainder by strong aqua regia, mixed with a little common salt, evaporation to dryness and leaching with water. The solution is freed from traces of the oxide of iridium by mixing with sodium carbonate, evaporating to dryness, igniting and dissolving the platinum with aqua regia. The alcoholic filtrate containing palladium, rhodium, iron, and copper, with small quantities of platinum, iridium and manganese, is saturated in a bottle with hydrogen sulphide and allowed to stand twelve hours. It is then filtered and the filtrate evaporated, any sulphides precipitating being added to mass of sulphides already separated. This precipitate, consisting of sulphides of palladium, rhodium, iridium and copper, is roasted in a platinum crucible and digested with strong hydrochloric acid. The acid solution, containing palladium and copper is evaporated with chloride of ammonium and nitric acid. From this mass alcohol dissolves the copper and a trace of palladium (to be precipitated with cyanide of mercury). The roasted mass, insoluble in the acid, is fused with potassium bisulphate and leached with water to remove the rhodium. The remainder is treated with aqua regia which dissolves platinum and leaves iridium. The liquid from which the metallic sulphides were precipitated, containing iron, with small quantities of iridium and rhodium, and a trace of manganese, is treated with nitric acid and the iron precipitated by ammonia. This precipitate, containing oxides of iridium and rhodium, is reduced by hydrogen and the iron dissolved in hydrochloric acid. The iridium and rhodium remaining, are separated as before. The filtrate from the iron precipitate is evaporated with sodium carbonate and gently ignited. Hydrochloric acid dissolves out manganese and leaves the oxides of rhodium and iridium.

Method of Claus.

The mechanical preparation, solution in aqua regia and determination of osmium, as by Berzelius. The treatment of the aqua regia solution is as follows. It is evaporated to dryness and heated to 140°—150° for some time. A little hydrochloric acid is added and the whole is dissolved in water. This is mixed with sal-ammoniac and the precipitate filtered off and washed with dilute sal-ammoniac solution and alcohol (80 %). Platinum is got from the precipitate by ignition and may be separated from any iridium by solution in aqua regia. The filtrate from the platinum is treated with chlorine and evaporated to dryness. The dry mass is powdered and washed with alcohol (80%) and filtered till the alcohol comes through colorless. This filtrate contains iron and copper. The mass is now washed with dilute solution of sal-ammoniac till the liquid runs through colorless. Rhodium and palladium are dissolved; platinum and iridium remain. The solution is evaporated to dryness and the dry mass ignited and weighed. From this the palladium is dissolved by aqua regia, the solution evaporated nearly to dryness and a drop of caustic soda solution added; the palladium is precipitated by cyanide of mercury. The platinum and iridium residue is heated with water; aqueous sulphydric acid added to convert tetrachloride into trichloride of iridium, and the liquid concentrated and mixed with strong solution of ammonium chloride. The precipitated platinum is washed free from iridium by a strong solution of sal-ammoniac.

Method of Deville and Debray.

The sand is determined by fusion of a portion of the ore with a carefully weighed portion of silver in the presence of powdered borax. To determine the iridosmine another portion is digested with aqua regia and the weight of the sand as found before deducted from the insoluble residue. The acid solution is evaporated and mixed with alcohol and amonium chloride. The precipitated platinum and iridium are ignited and separated by aqua regia. The filtrate from the platinum and iridium is evaporated until a great part of the ammonium chloride crystallizes out—a little iridium and platinum is then deposited and is treated with that above. The solution still contains palladium, rhodium, iron, copper, and gold. The alcohol is driven off and the ammonium chloride decomposed by nitric acid.

The solution is evaporated to dryness and the residue dried in a porcelain crucible, moistened with a solution of ammonium sulphide, two or three parts of flowers of sulphur added and then the whole dried and heated to bright redness. The weighed contents, consisting of metallic palladium, gold, and rhodium, sulphide of iron ($F_3 S_4$) and sulphide of copper ($Cu_2 S$), are digested with strong nitric acid at 70°, which dissolves palladium, iron and copper. The solution is evaporated to dryness and ignited. Dilute hydrochloric acid dissolves the iron and copper, which are separated as usual. The gold and rhodium are separated by weak nitro-muriatic acid.

METHODS FOR ANALYSIS OF IRIDOSMINE.

Method of Berzelius.

The iridosmine is ground in a mortar and heated strongly, with an equal weight of nitre, in a porcelain retort. The vapor of osmic oxide is caught in dilute ammonia. More osmium is got from the mass by leaching with water and heating the solution with hydrochloric acid to drive over the osmium. The undissolved portion is likewise freed, as far as possible, from osmium by heating with acid. The chloriridiate of potassium, freed by water and alcohol from chromium, is ignited in a porcelain retort with sodium carbonate—any volatilized osmium being caught. The residue is treated with water and the insoluble oxide of iridium freed from platinum by aqua regia and from rhodium by fusion with potassium bisulphate. The osmium is got from solution by digestion with mercury.

Method of Deville and Debray.

The iridosmine is disintegrated by fusion with zinc and then separated by dilute acid. It is mixed with peroxide of barium or peroxide and nitrate of barium and heated in a silver crucible. The cooled mass is transferred to a larger dish, mixed with hydrochloric acid and nitric acid, heated till all osmium is driven off, and evaporated to dryness. The residue is digested with warm water and a little acid and the solution decanted off. The unattacked iridosmine is weighed and accounted for. The barium is precipitated from the solution by titration with sulphuric acid, and, from the filtrate, platinum, iridium, and ruthenium are precipitated by sal-ammoniac, and reduced. From this reduced mass platinum is removed by aqua regia. Ruthenium is separated by fusion with nitrate and hydroxide of potassium and solution in water. The rhodium, with iron and copper, remains in the filtrate from the iridium, platinum, and ruthenium. These are separated by the same methods as given under Deville and Debray's method for native platinum. The osmium is determined by loss.

Method of Wœhler.

The iridosmine is ignited with common salt in a stream of moist chlorine. Some of the osmium passes over into the receiver or solution of hydroxide of calcium. The mass in the tube is leached with water and the solution distilled with nitric acid to free it from osmium. To the remaining concentrated solution chloride of potassium is added, and most of the iridium precipitated. The remaining solution is evaporated with sodium carbonate, ignited, and washed free from alkalis by hot water. The black powder is reduced by hydrogen, sodium hydroxide removed by water and iron by hydrochloric acid. The small amount of platinum present is removed by dilute aqua regia. The remaining iridium is then freed from ruthenium and rhodium; the first by fusion with hydroxide and chlorate of potassium, the latter by fusing with bisulphate of potassium. The osmium is got from solution by mixing with hydroxide of calcium and boiling with an alkaline formate. The osmium is then ignited under hydrogen and weighed.

The following method, which is the one used in making the analyses reported in this paper, is the result of repeated experiments to get one which would answer for very small samples of the ore and at the same time be as expeditious as possible while being reasonably accurate. Consequently those methods which required long standing to complete precipitation or involved slow and tedious filtration, although often tried, were not used. Wherein suggestions have been received from the works of others and where their methods have been modified to suit the present circumstances, will be readily seen without specific reference in the body of the method. It is with pleasure that I also acknowledge the kind suggestions and interest of Professor Mallet and Professor Dunnington. To Mr. Kunz I am greatly indebted for the samples of the ore which were collected by himself from many quarters of the earth.

METHOD OF ANALYSIS OF PLATINUM ORES.

Mineralogical Examination.

With a microscope magnifying seventy diameters I examined the physical appearance of the different kinds of grains. Color, general shape, condition of edges and angles, whether sharply angular or rounded, presence or absence of regular geometric forms or faces, capability of transmitting light and any other properties which could be seen were noted. The sizes of the grains were determined by the use of an eye-piece micrometer. The color of the grains of native platinum was distinctive and often the grains of iridosmine could be distinguished by the presence of hexagonal plates. The platinum grains were often seen colored by a film of oxide of iron, as were the grains of gold which were occasionally present. Quartz was usually present and was distinguished without trouble, except in the case of grains having colors like garnet and topaz. The quartz and garnet were distinguished by their difference in specific gravity, for which purpose a solution of cadmium borotungstate was used, which had a specific gravity higher than the quartz grains and lower than the garnet. This determination had, usually, to be made under a strong magnifying glass, because of the small size of the grains. The quartz and topaz were distinguished by their different degrees of hardness, for which purpose a small piece of hard wood was made smooth on the end and used to rub the fine grains against the smooth face of a quartz crystal. Grains of iron oxide, which were often present, were told by their color, lustre, magnetic properties, regular geometric forms, where these properties were distinctive, and by fusion with acid sulphate of potassium and addition of potassium ferrocyanide. The presence of titanium was told by fusion with acid sulphate of potassium and addition of hydrogen dioxide which gives a characteristic and delicate reaction in the yellow color produced.

Separation of Gold.

From a weighed portion of the ore (*See Note below),

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* The methods which have been given in outline in this paper usually require from ten to fifteen grammes for a complete analysis, and different portions are used for determination of the gold and siliceous matter, etc., and the platinum metals proper. The samples I had, however, never allowed more than a gramme and a half, and in several instances only seven-tenths of a gramme. This necessitated the use of but one portion for the entire analysis, and even then, the amount was small, especially for the determination of the iridosmine present.

the gold was picked out by hand, if in grains of sufficient size to make this practicable. A large magnifying glass was found to be of service, and the end of a feather, used instead of a pair of needles, facilitated the separation. The weight of the gold was in this way determined directly.

If this method was not practicable, I removed the gold by amalgamating it with pure mercury, using a solution of potassium cyanide to keep the surface clean and to prevent the sand and platinum grains from adhering to the mercury. I then washed the mercury and drove it off by heat, weighing the residual gold. The ore was washed free from the alkaline salts and treated as follows:

Separation of Sand, Etc.

From the ore remaining from the gold the sand, etc., was removed by hand if practicable. Otherwise the inner surface of a small Beaufaye crucible was glazed with melted borax, and into it was put, for one part of ore by weight, four to five parts of pure silver (accurately weighed) in a state of fine sub-division. The ore was added and all covered by powdered borax glass of approximately the same weight as the silver. On top of the borax I put one or two small pieces of wood charcoal to prevent any possible oxydation. The crucible was then covered, placed within a larger covered crucible to prevent too high heat or danger of overturning, and put into a furnace and kept at such a heat as rendered the borax quite fluid for several minutes. I shook or jarred the crucible two or three times during the heating to facilitate the separation of the silver. After cooling, the crucible was broken open and the "button" freed from the borax as completely as possible by hammering. The last traces of borax were removed with dilute hydrochloric acid. The "button" was then weighed and this weight subtracted from the combined weight of ore and silver gave the weight of the sand, etc., removed. I treated the "button" with a minimum of slightly warmed, pure nitric acid, diluted with its own bulk of water, until the silver was completely dissolved. Care was exercised to permit of the entrance of no chlorides. The residual platinum metals were washed by decantation and filtration, first with water acidified with nitric acid and then with water alone, until I could obtain no evidence of silver in the wash water. The filtrate and wash water were put into a flask and hydrochloric acid added until the precipitation of the silver was complete. After vigorous shaking to hasten separation, the flask was left for several hours in a comparatively warm place, protected from the light. The precipitated chloride of silver was washed by decantation and filtration with water acidified with nitric acid. The filtrate, which contained a small portion of the metals, was evaporated on the water bath to a small bulk and added to the solution obtained by treatment of the platinum metals with aqua regia.

Analysis of the Platinum Grains.

The metals, which remained after the silver was dissolved, were put into a glass retort of 500^{cc} capacity, about the neck of which was a condenser jacket made of rubber tubing. The retort neck was connected by a ground joint with one of two openings of a spherical receiver, to the other opening of which, by a similar joint, a bent glass tube was fitted, dipping by its free end under a strong solution of caustic potash; this tube was widened to prevent the potash solution being drawn into the receiver. I connected the vessel, holding the caustic potash, with a bottle containing broken bits of pumice saturated with strong alcohol, to prevent the escape of free chlorine. The receiver rested in a bath of cold water and the retort on a sand bath. Into the retort I put for one part by weight of the metals six parts of concentrated hydrochloric acid and two parts of fuming nitric acid, and heated carefully, avoiding all rapid evolutions of gas likely to carry any liquid over mechanically, until three-fourths of the acid had distilled over. The retort was then allowed to cool somewhat and sufficient hot water added to dissolve whatever had been rendered soluble by the acid. After having stood long enough for all insoluble matter to settle completely, I drew off the liquid by means of a pipette, being careful to remove only a clear solution, Acid as before was put into the retort, the proportion of the metals remaining unattacked being judged of approximately and distilled in the same manner. This was repeated until the acid no longer attacked the metals. The retort was then allowed to cool down, and with as much expedition as possible the contents of the receiver were transferred back to the retort and redistilled to remove any traces of the liquid which might have been carried over mechanically. By this treatment all the osmium of the ore, except that contained in the iridosmine, was oxydized to tetroxide ($Os O_4$) and distilled over as such. All the other metals, except the iridosmine, were dissolved in the aqua regia.

After the apparatus had cooled, the potash solution and contents of the receiver were poured together into a beaker as rapidly as possible, care being taken to have caustic potash present in such an amount as to render the liquid strongly alkaline. From this the osmium was precipitated by hydrogen sulphide in excess. Sulphur at times was separated, but usually dissolved in the alkaline sulphide formed or else was removed, after the precipitate was thoroughly dried, by solution in carbon bisulphide. That the osmium was precipitated as osmium bisulphide ($Os S_2$) was proven by two analyses of the precipitate. Several hours were allowed for the precipitate to separate and settle, and then the liquid was decanted off and the precipitate washed by decantation and filtration with hot water containing ammonium sulphide. The precipitate, after drying in the air bath at 110°C was removed as completely as possible from the filter paper and put into a weighed porcelain crucible; the filter paper, after incineration, was added and the whole cooled in a dessicator and weighed. There was manifestly some loss of osmium by this method, as indeed there is by any method, but care was exercised to reduce the loss as much as possible.

The contents of the retort were washed into the beaker which contained the portions previously removed and the iridosmine was filtered, washed thoroughly with hot water, dried at 110°C and weighed.

The filtrate and wash water, to which was added the filtrate from the chloride of silver got from the "button," were evaporated to a small bulk and allowed to cool—this latter to prevent precipitation of palladium—and an excess of a saturated solution of ammonium chloride was added. This was allowed to stand several hours. Most of the platinum was thus precipitated together with a small amount of iridium. This precipitate was filtered off and washed, first, with a diluted solution of ammonium chloride —saturated solution of amonium chloride one part by volume and water three parts—and then, with 80°/₀ alcohol until iodide of potassium gave no indication of the presence of palladium in the filtrate. The precipitate was dried at 100°C., ignited under a stream of hydrogen and weighed, the ignition being repeated until the weight was constant. The platinum was dissolved out from this by diluted aqua regia and filtered, the residual iridium being dried, was ignited under hydrogen and weighed. I determined the platinum by difference.

The mixed filtrate and washing liquid from the double chlorides were concentrated to a small bulk on the water bath and boiled with concentrated nitric acid, added in small portions to prevent any large excess, until all the chloride of ammonium was decomposed. The remaining liquid was then evaporated to dryness in a small porcelain dish, pulverized, rubbed up with a dilute solution of ammonium chloride, filtered and washed with the same solution until no palladium or copper could be detected in the filtrate.*

The filter, containing the remainder of the platinum and iridium, with that portion of the iron which oxidized in the evaporation to dryness, was dried at 100°C. and ignited under hydrogen. The reduced metals were digested with dilute aqua regia to dissolve out platinum and iron. The residual iridium was filtered off, washed, dried, ignited under hydrogen and weighed. The filtrate was evaporated to dryness, dissolved in dilute pure sulphuric acid, transferred to a flask fitted with a Bunsen valve, and pure zinc added. After precipitation of the platinum and reduction of the iron—care being taken that no zinc was left undissolved—the contents of the flask were filtered and washed under carbon dioxide. The platinum was ignited under hydrogen and weighed; the iron was determined by titration with a standardized solution of permanganate of potassium.

The filtrate from the platinum, iridium and iron, containing the palladium, rhodium, copper and remaining iron, was evaporated to a small bulk, boiled with strong nitric acid to decompose all excess of ammonium chloride, and evaporated to dryness on the water bath. The dried mass having been dissolved in dilute hydrochloric acid, I precipitated the rhodium and palladium by pure zinc, being careful to have the solution distinctly acid at the last,

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*Of course the salts of platinum and iridium are not entirely insoluble in this washing fluid, but the amount dissolved was very small and was disregarded.

and then, having filtered and washed the metals, I ignited them repeatedly under hydrogen until their weight was constant. The palladium was dissolved in diluted aqua regia, filtered and evaporated to dryness to get rid of all acid. Some rhodium was also dissolved, but did not injure the determination of palladium. The dry palladium salt was dissolved in water and an excess of a saturated solution of mercuric cyanide added to precipitate palladium. After standing several hours, the yellowish-white precipitate of palladious cyanide was filtered off, washed, ignited, first over a strong blast in the air and then over a Bunsen burner under hydrogen and weighed. The rhodium was determined by difference.

The filtrate from the palladium and rhodium, which contained the iron and copper, was treated with nitric acid to change the iron to the ferric condition, and this was then precipitated by ammonium hydroxide, filtered and washed repeatedly with water containing ammonia. (I know that this does not completely separate all the copper, but in several trials to further separate it by resolution and re-precipitation of the iron I found such a small trace of copper that it would not perceptibly alter the result). The iron was then dissolved in diluted sulphuric acid and determined volumetrically as before.

The filtrate from the iron was put into a measuring flask, made very faintly acid and the flask filled to the mark with water. The copper was then determined by colorimetric test with ammonium hydroxide, using a dilute solution of copper sulphate of known strength as a standard.*

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*Since the analyses were made I have determined that this method for the separation of palladium, rhodium, iron and copper is not strictly accurate, in that some of the copper is likely to be precipitated by the zinc along with the palladium and rhodium. In so far as this was done, the copper was determined as rhodium. This error is not of great moment, however, for two reasons—first, because of the small amounts of either

Analysis of the Iridosmine.

I mixed the iridosmine with three or four times its bulk of well decrepitated powdered salt in a porcelain boat and heated the mixture in a glass tube to a dull red heat, under a slow stream of moist chlorine. For this purpose I used the following apparatus. For the generation of the chlorine, I used a 700^{cc} round bottom glass flask, which rested on a sand bath, and which was provided with a safety thistle tube and a tube connecting with a water bottle, through the water in which the gas was passed. Into the flask, I put an excess of coarsely granulated manganese dioxide and sufficient concentrated hydrochloric acid to yield a slow stream of chlorine for three or four hours. From the water bottle, the gas was conducted by a tube into the hard glass tube in which was heated the iridosmine. This hard glass tube was bent to enter the neck of a retort, where it fitted by a ground joint. I used a small gas furnace for heating. The receiver rested in a bath of cold water and was connected with glass tube, fitted by ground joint to a flask containing a strong solution of caustic potash.

After placing the boat in the tube and before the chlorine was permitted to enter, I heated the tube quite hot, and so, when it was allowed to cool down after the operation, the chlorine was cut off before it had cooled completely. This seemed to prevent the tube's cracking and so increased its length of service. After the chlorine had been started, the mass in the tube was heated to dull redness and continued at that temperature, until the chlorine ceased being

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rhodium or copper present; second, and chiefly, because very *little* copper was so precipitated: for instance, in Sample "C," from Russia, two per cent. and more of copper was found and no rhodium, either as rhodium itself or as copper weighed as rhodium. However this slight error may be avoided by determining the copper in the filtrate from the precipitated palladious cyanide.

absorbed. By this process, the osmium was volatilized, mainly in the form of osmic oxide, and was caught in the colder end of the tube, the receiver and, the last traces, in the caustic potash solution. The other metals, together with traces of the osmium, remained in the boat as soluble double chlorides of the metal and sodium.*

After cooling, and removal of the boat, the contents of the tube, receiver and caustic potash flask were washed out into the same beaker and set aside to have added to the mixed liquid the osmium subsequently obtained.

The mass in the boat was dissolved in a minimum of hot water and filtered. The part remaining unattacked was not retreated, but was weighed and the amount deducted from the weight of the iridosmine taken, thus giving the amount acted on by the chlorine; from this, the weights of the metals, found by subsequent analysis, were calculated as though the entire mass had been decomposed. This materially lessened the time consumed in the operation and lessened the chances of loss. The filtrate, containing the double chlorides, was put into a retort, which was connected and fitted in a similar way to that used to decompose the metals by aqua regia. To it was added about one-fourth its volume of a mixture of concentrated nitric acid—four parts—and strong hydrochloric acid—one part.†

By distilling this mixture to one-fourth its volume, the osmium was volatilized and caught, as already described, and then added to the osmium solution obtained from the moist chlorine treatment. From this the osmium was precipitated and determined as described already. The concentrated solution left in the retort was washed out

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*I could find no evidence of the volatilization of ruthenium along with the osmium.

†The small proportion of hydrochloric acid used was due to the presence of chlorides in the solution to be treated.

with hot water, evaporated to a small bulk on the water bath, and, after the addition of an excess of a saturated solution of ammonium chloride, was allowed to stand several hours. The precipitated double chlorides of iridium and ammonium, and platinum and ammonium were filtered off and washed with a strong solution of ammonium chloride till it came through colorless. The precipitate was then treated, as before described, to separate and determine the iridium and platinum. The filtrate and washing water which contained the rhodium, ruthenium, iron, and copper, was boiled for a short time with an excess of nitrite of potassium, sufficient carbonate of potassium being added to keep the solution slightly alkaline, and then evaporated to dryness on the water bath in a small porcelain dish. The dry mass, ground to a very fine powder, was transferred to a flask fitted with a reflux condenser, and digested in boiling absolute alcohol for a few minutes. The ruthenium salt present readily dissolved under these conditions, and the boiling needed to be repeated only once or twice with fresh alcohol. The ruthenium was separated by filtration, washing with absolute alcohol until none of the metal could be detected in the washing liquid when colorless sulphide of ammonium was added—with ruthenium this gives a fine crimson color. This filtrate was evaporated to dryness, water and hydrochloric acid added and the ruthenium precipitated by zinc, filtered off, washed, ignited under hydrogen and weighed. The filtrate from the ruthenium was examined for iron and copper in the same way as described already. (A little iron was found occasionally but no copper—the same objection may be made to this method here as is made elsewhere and the same remedy applied; but it is very doubtful if any copper would even then be found.)

The mass which was insoluble in the absolute alcohol contained the rhodium and most of the iron and copper when present. It was dried, ignited in a weighed crucible in the air, washed free from alkali, and ignited under hydrogen until the weight was constant. The iron and copper were dissolved out by dilute nitric acid and determined as before described. The rhodium was reignited and weighed.

RESULTS OF MINERALOGICAL EXAMINATION.

A. Russia.[*]

Platinum.—Large grains, non-magnetic and of irregular shape.

Size: $.39^{\text{mm}} \times .61^{\text{mm}}$ to $1.61^{\text{mm}} \times 2.05^{\text{mm}}$.

Gold.—One grain of moderately large size: $.51^{\text{mm}} \times .64^{\text{mm}}$.

Quartz.—Two pieces were found: $.5^{\text{mm}} \times .6^{\text{mm}}$.

Magnetite.—Two small pieces: $.11^{\text{mm}} \times .11^{\text{mm}}$.

C. Russia.

Platinum.—Large grains coated with yellow clay.

Size: $.47^{\text{mm}} \times .62^{\text{mm}}$ to $2.9^{\text{mm}} \times 3.8^{\text{mm}}$.

E. Ecuador.

Platinum.—Magnetic, irregular flat grains, resembling scales. On ignition turns red brown in color and loses its magnetic character.

Size: $.20^{\text{mm}} \times .31^{\text{mm}}$ to $.79^{\text{mm}} \times 1.10^{\text{mm}}$.

Gold.—Flat scales and irregular grains.

Size: $.19^{\text{mm}} \times .21^{\text{mm}}$ to $.47^{\text{mm}} \times .57^{\text{mm}}$.

Titanic Iron Ore.—Small grains, not many in number—bright and specular—showing a few rhombohedral faces.

Size: $.16^{\text{mm}} \times .16^{\text{mm}}$.

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[*] The original labels of the samples.

Two pieces of rock were observed—black and yellowish-brown—magnetic, $1.10^{mm} \times 2.10^{mm}$.

F. BRITISH COLUMBIA.

Platinum.—Large grains.

Size: $.90^{mm} \times 1.00^{mm}$ to $1.7^{mm} \times 2.5^{mm}$.

There was no material other than these grains of platinum present.

H. CALIFORNIA.

Platinum.—Some of the grains were magnetic, others not. The grains were of irregular shape, many flat. They had a metallic lustre. A few were stained with iron oxide.

Size: $.13^{mm} \times .22^{mm}$ to $.24^{mm} \times .29^{mm}$.

Iridosmine.—Flat, rounded and oblong tables. There were no hexagonal plates. Some of the grains were bright, some dull. A few were tinged by iron oxide.

Size: $.11^{mm} \times .11^{mm}$ to $.16^{mm} \times .22^{mm}$.

Quartz.—Quite a large number of grains, most of which were colorless and transparent, but some few light yellow and yellowish-brown, and a few others of greenish hue.

Size: $.08^{mm} \times .10^{mm}$ to $.10^{mm} \times .13^{mm}$.

Garnet.—A few grains of reddish-brown color.

Size: $.09^{mm} \times .10^{mm}$.

Specular Iron.—Irregular and angular grains, showing, on some, rhombohedral faces. Grains, shining.

Size: $.09^{mm} \times .09^{mm}$.

Magnetite.—Dull and rounded grains.

Size: $.10^{mm} \times .10^{mm}$ to $.21^{mm} \times .23^{mm}$.

Mercury.—Globules, which had evidently been used to remove gold.

I. URALS—RUSSIA.

Platinum.—Non-magnetic. Rough and irregular in shape. Clinging to a few grains was a light yellow organic matter, which, on ignition, yielded an alkaline reaction. A few grains had also a yellow ferruginous clay on their surface.

Size: $.48^{mm} \times .72^{mm}$ to $.78^{mm} \times .91^{mm}$.

Quartz.—A very few grains.

J. OREGON.

Platinum.—Much of it magnetic—grains small—both rounded and angular. Many were colored yellow by oxide of iron.

Size: $.08^{mm} \times .08^{mm}$ to $.11^{mm} \times .19^{mm}$.

Gold.—A few grains. Most of them coated by iron oxide.

Size: $.11^{mm} \times .16^{mm}$.

Garnet.—Angular grains. Light brownish-red.

Size $.09^{mm} \times .09^{mm}$.

Topaz.—A few very small, rounded grains of a light lemon yellow color.

Size: $.08^{mm} \times .08^{mm}$.

Specular Iron.—Some of it dull and some bright and shining.

Size: $.10^{mm} \times .13^{mm}$.

K. OREGON.

Platinum.—Non-Magnetic—the grains bright and shining, irregular in shape; the majority of them having sharp edges.

Size: $.28^{mm} \times .33^{mm}$ to $.59^{mm} \times .80^{mm}$.

Iridosmine.—Some flat, rounded grains and a few apparently perfect hexagonal plates.

Size: $.56^{mm} \times .60^{mm}$.

Quartz.—Mainly colorless, transparent, angular grains, a few, however, rose colored or light yellow.

Size: $.17^{mm} \times .24^{mm}$.

Magnetite.—A few small pieces, reddish-brown on surface, as though changing to limonite.

Size: $.15^{mm} \times .17^{mm}$.

A few pieces of a clay-like matter, which, on ignition, gave odor of burning organic matter.

A very few small grains of gold were present.

L. Republic of Columbia.

Platinum.—The sample consisted of five large grains and two smaller ones. There was no visible evidence of anything save platinum, except on two or three of the larger grains, in the rough places, a little siliceous matter was collected. The grains were rounded on the edges and of irregular shape.

Size: Small grains, $2.^{mm} \times 2.5^{mm}$.
Large grains, $3.^{mm} \times 4.5^{mm}$ to $5.^{mm} \times 5.^{mm}$.

M. Republic of Columbia.

Platinum.—The grains were very small and of irregular shape, coated in some instances by oxide of iron, giving a parti-colored effect.

Size: $.06^{mm} \times .06^{mm}$ to $.08^{mm} \times .14^{mm}$.

Iridosmine.—A few flat, rounded grains were the only visible evidences of its presence.

Size: $.07^{mm} \times .07^{mm}$.

Gold.—A very few gold grains of minute size.

Size: $.05^{mm} \times .06^{mm}$.

Quartz.—Colorless and light yellow; the grains were of irregular shape, some being rounded on the edges.

Size: $.18^{mm} \times .23^{mm}$.

Garnet.—A few grains of a clear brownish-red.

Size: $.07^{mm} \times .08^{mm}$.

A piece of slightly ferruginous sand-stone and a few pieces of organic matter were present.

N. OREGON.

Platinum.—Magnetic. The grains were light steel gray, small, of no regular shape, some rounded, some long and slender. A few were very slightly tinged with iron oxide.

Size: .05^{mm} × .20^{mm} to .18^{mm} × .20^{mm}.

Iridosmine.—Many flat, rounded grains. Some imperfectly hexagonal.

Size: .08^{mm} × .08^{mm} to .20^{mm} × .20^{mm}.

Quartz.—Colorless, milky, and light green. Some of the grains were rounded, others not.

Size: .10^{mm} × .11^{mm} to .20^{mm} × .22^{mm}.

Topaz.—The grains were rounded and light lemon yellow.

Size: .10^{mm} × .11^{mm}.

Garnet.—A few grains of a light brownish-red, angular.

Size: .09^{mm} × .11^{mm}.

Iron Oxide.—Both magnetite and specular varieties present. Some octahedra were seen. Other grains were irregular or rounded. Some lustrous, others dull.

Size: .11^{mm} × .13^{mm} to .15^{mm} × .16^{mm}.

O. BOGUS GOLD DUST.

Platinum.—Non-magnetic, light steel gray grains, of a shining, metallic lustre. The grains were very rough and irregular, many being flat and wrinkled like foil, although there was no appearance of their having been actually worked. Some grains were stained by iron oxide.

Size: .35^{mm} × .71^{mm} to 1.4^{mm} 4.5^{mm}.

Gold.—A very few grains, so minute and so few as to prevent quantitative determination.

P. REPUBLIC OF COLUMBIA.

Platinum.—Non-magnetic grains, of large size, with shining metallic lustre, irregular in shape and with rounded edges.

Size: .63^{mm} × .63^{mm} to 3.^{mm} × 3.^{mm}.

Iridosmine.—Only a few flat, rounded grains were seen. No hexagonal plates.

Size: $.5^{mm} \times .5^{mm}$.

Gold.—Rounded grains and scales. A few pieces of gold-bearing quartz were present.

Size: $.54^{mm} \times .71^{mm}$ to $1.7^{mm} \times 1.9^{mm}$.

Quartz.—Colorless, irregular shaped, angular grains. A few pieces of the milky variety.

Size: $1.8^{mm} \times 2.0^{mm}$.

Iron Oxide.—Both magnetite and specular iron present. Several octahedra were noticed and several rhombohedral faces.

Size: $.6^{mm} \times .8^{mm}$.

One or two fragments of a gray gold-bearing rock were seen.

Q. REPUBLIC OF COLUMBIA.

Platinum.—Rounded and irregularly shaped grains, light steel gray in color and occasionally stained yellow by iron oxide.

Size: $.14^{mm} \times .14^{mm}$ to $.26^{mm} \times .32^{mm}$.

Iridosmine.—A few flat, rounded grains.

Size: $.32^{mm} \times .39^{mm}$.

Gold.—A few small and irregular grains.

Size: $.13^{mm} \times .18^{mm}$.

Quartz.—Colorless, irregular fragments and transparent prisms. The amethystine variety was also present. Rhombohedral faces were seen.

Size: $.10^{mm} \times .14^{mm}$ to $.22^{mm} \times .24^{mm}$.

Garnet.—Irregularly shaped grains of a light brownish-red color.

Size: $.12^{mm} \times .16^{mm}$.

Iron Oxide.—Titaniferous magnetite. Octahedra and rhombic dodecahedra were present. Most of the grains were of irregular shapes.

Size: $.13^{mm} \times .13^{mm}$ to $.14 \times .16^{mm}$.

R. OREGON.

Platinum.—The most of it non-magnetic. Some was shining and with metallic lustre, some was dull; in color a light steel gray and of irregularly rounded forms.

Size: $.08^{mm} \times .10^{mm}$ to $.16^{mm}$ to $.19^{mm}$.

Iridosmine.—Many flat, rounded plates.

Size: $.21^{mm} \times .34^{mm}$.

Quartz.—Colorless, smoky, yellowish, greenish, and rose colored grains were present. Irregular in shape and with rounded edges.

Size: $.08^{mm} \times .09^{mm}$.

Topaz.—Rounded, lemon yellow grains.

Size: $.09^{mm} \times .09^{mm}$.

Garnet.—Brownish-red, irregularly rounded grains.

Size: $.08^{mm} \times .08^{mm}$.

Iron Oxide.—Magnetite. Black, rounded grains, with shining metallic lustre, some being dull, however.

Size: $.10^{mm} \times .11^{mm}$.

U. OREGON.

Platinum.—Many of the grains were magnetic. In shape irregular and rounded. Some shining, others were dull. Some were tinged yellow by oxide of iron.

Iridosmine.—Flat, rounded grains. Some were imperfect hexagonal plates.

Size: $.15^{mm} \times .16^{mm}$ to $.23^{mm} \times .24^{mm}$.

Quartz.—A few grains of irregular form and of slight yellow color.

Size: $.13^{mm} \times .13^{mm}$.

Garnet.—Almandite variety. The color was a fine red, though a few grains were yellowish-brown.
Size: .10^{mm} × .10^{mm}.

Iron Oxide.—Magnetite. Rounded, black grains. Some with a metallic lustre and some dull.
Size: .13^{mm} × .13^{mm}.

V. OSMIUM* (*sic*) FROM REFINED PLATINUM.

Iridosmine.—Light steel gray grains of bright metallic lustre, and of irregular shapes. Some hexagonal tables were present.
Size: .12^{mm} × .13^{mm} to .56^{mm} × .67^{mm}.

Quartz.—Colorless, rose, and light yellow varieties. Some of the grains were sharply angular, others worn smooth. There were present a few ends of prisms showing rhombohedral faces.
Size: .07^{mm} × .08^{mm}.

Topaz.—Rounded, light lemon yellow.
Size: .05^{mm} × .06^{mm}.

Garnet.—Brownish-red, irregular and sharply angular grains.
Size: .06^{mm} × .07^{mm}.

Iron Oxide.—Titaniferous magnetite. Dull black, rounded grains and octahedra, with a few imperfect rhombic dodecahedra.
Size: .10^{mm} × .13^{mm}.

Results of Chemical Analysis.

I give the following tabulated statements of the results of my analysis of the samples. The first table gives the results of analysis of the crude ore. The second table gives the results of analysis of the iridosmine found in the samples of crude ore analysed. Not all of the samples

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*The sample was *Iridosmine.*

furnished sufficient iridosmine to be analyzed. Indeed, in no case was there enough for satisfactory work. The iridosmine from the sample "P" would have been analyzed, but was lost, unfortunately, by an accident. Sample "H" contained some gold amalgamated with the globules of mercury present, but neither is indicated in the table of results, for the reason that the mercury had been added to remove gold, and the amount of gold found was an unknown portion of the total amount occurring in the crude ore.

Sample "L," from the Republic of Columbia, yielded me 2.107% of osmium although I found but 1.159% of iridosmine. It might be supposed that the relatively large amount of osmium was due to other metals being mechanically carried over into the receiver, but I hardly think so. I exercised care in this regard and, furthermore, find that Berzelius reports a similar case (See Watt's Dictionary, Vol. IV, p. 679) in which he found 1.03% of osmium and no iridosmine. Indeed there is no evidence that the amount of osmium obtained by treatment with aqua regia is in any definite ratio to the amount of iridosmine present.

I could detect no relation between the magnetic properties of the grains and the amount of iron found by analysis. Indeed some of the samples poorest in iron were as markedly magnetic as those containing more, and, some showing large amounts of iron were non-magnetic or only slightly magnetic.

It will be seen that samples from the same (general) region, differ widely in the results of analysis. For instance the four samples from the Republic of Columbia show percentages of platinum ranging from 38% to 90%; Russian samples varied from 49% to 84% of platinum; and Oregon samples varied from 24% to 94% of iridosmine.

As a general rule the samples from the Western parts of the United States showed high percentages of iridosmine.

Most of the samples from South America were low in iridosmine and the same is true of the Russian samples.

I think it is very doubtful if the high percentages of rhodium found in most of the iridosmine residues are correct. Minute amounts of iridium are dissolved in the solution of ammonium chloride used to wash the precipitated iridium and platinum salts. In the analysis of several grammes of iridosmine this error would be inappreciable, but it shows decidedly in the present case where the amount of iridosmine decomposed was about .20 grammes on the average. For instance in sample "V" I had a little more than a gramme of iridosmine to work with and found less than one per cent. of rhodium. Of course all the iridium dissolved was afterwards weighed as rhodium.*

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*Since writing the above I have made an analysis of the rhodium (?) residues from the iridosmine. It was not possible to do this with any one residue of rhodium, but by combining all of them, enough was obtained to permit of analysis. I found only 8.61 per cent of rhodium present, the rest being iridium. The iridium was evidently dissolved as I supposed, and the percentages given in the table of the iridosmine results will need to be modified accordingly.

Results of the Chemical Analysis of the Crude Platinum.

No.	Locality.	Pt.	Ir.	Os.	Pd.	Rh.	Fe.	Cu.	Au.	I. O.	Sand, etc	Total per cent.
A	Russia	83.984	1.577	....	.221	.162	7.573	.516	Trace.	4.412	....	98.445
C	Russia	78.872	.289	Trace.	Trace.	....	12.847	2.395	....	2.849	1.904	99.156
E	Ecuador	85.109	.335	....	1.200	.746	8.195	.460	1.890	.642	1.583	100.160
F	British Columbia	79.130	2.969	....	.598	.360	10.493	1.838	....	4.108	....	99.496
H	California	52.927	.271	.418	1.150	.791	5.041	.352	....	20.588	16.950	98.488
I	Urals—Russia	48.920	.354	Trace.	.981	.300	4.033	Trace.	....	44.158	.559	99.305
J	Oregon	39.047	1.015	1.034*	.890	.439	3.769	.327	.969	49.669	2.841	100.
K	Oregon	.825	....	....	.509	....	....	....	....	97.306	1.237	99.877
L	Republic of Columbia	90.654	.685	2.107	.618	1.349	1.517	.729	....	1.159	.233	99.051
M	Republic of Columbia	37.802	1.343	2.328*	.870	1.241	1.966	.486	Trace.	47.013	6.921	100.
N	Oregon	54.272	.779	2.058	.508	1.117	3.081	.508	....	20.968	14.496	97.787
O	"Bogus gold dust"	96.183	.571	....	.205	.132	.037	1.901	Trace.	.650	....	99.679
P	Republic of Columbia	52.114	.831	.878	.288	.362	3.218	....	1.803	38.173	1.602	99.269
Q	Republic of Columbia	72.641	.815	.326	.564	1.989	4.855	.285	.767	1.161	15.720	99.123
R	Oregon	46.711	.923	.633	Trace.	.097	4.225	.206	....	24.476	22.584	99.855
U	Oregon	43.480	.250	.240	.070	.250	3.690	.330	....	41.320	10.560	100.190
V	Osmium† (sic) from Refined Platinum	.470	Trace.	.250	....	.100	.170	.110	....	65.290	33.290	99.680

*Osmium determined by difference. †Really Iridosmine

Results of the Chemical Analysis of the Iridosmine found in the Crude Platinum.

No.	Locality.	Ir.*	Os.	Pt.	Rh.*	Ru.	Fe.	Total per cent.
H	California	19.787	45.231	1.175	32.918	....	....	99.111
I	Urals—Russia	12.512	51.589†	.293	32.644	2.962	....	100.
J	Oregon	33.852	44.142†	.435	20.306	....	1.265	100.
K	Oregon	31.252	50.324†	.749	16.912	.763	Trace.	100.
M	Republic of Columbia	33.524	53.959	Trace.	10.476	.952	Trace.	98.911
N	Oregon	35.389	43.784	Trace.	8.105	10.300	.420	97.998
R	Oregon	21.796	44.100	.487	27.884	1.431	....	95.698
U	Oregon	43.910	53.140	.770	1.450	.860	....	100.130
V	Osmium‡ (sic) from Refined Platinum	41.890	45.290	1.760	.770	11.950	....	101.660

*See foot note (page 29) †Osmium determined by difference. ‡Really Iridosmine.