

## THE CHEMICAL ANALYSIS OF IRIDOSMINES AND OTHER PLATINUM-METAL MINERALS

A. D. WESTLAND AND F. E. BEAMISH, *University of Toronto, Toronto,  
Ontario, Canada.*

### ABSTRACT

Some of the difficulties associated with the chemical separation and determination of the constituents of iridosmines are discussed and the methods of dissolution are reviewed. Applications of these procedures to the analysis of iridosmines from various world sources are made and the conclusion is reached that significant and hitherto unsuspected mineralogical data can be obtained by the use of accurate chemical analysis of micro crystals whose composition may differ considerably from that of the accumulation of crystals from a single deposit. These micro methods of analysis have revealed the presence of palladium in iridosmines; and the existence of minerals with higher and lower osmium contents than any hitherto reported.

### INTRODUCTION

Platinum, palladium, rhodium, iridium and osmium have been known for over 150 years and the sixth element of the family, ruthenium, for 112 years. These metals have been used commercially for much of this time but in spite of this fairly long history, the mineralogy of this group is relatively little known. The compounds, cooperite, PtS; braggite, (Pt, Pd, Ni)S; laurite RuS<sub>2</sub>; sperrylite, PtAs; potarite, PdHg; and stibio-palladinite, Pd<sub>3</sub>Sb; have been reported, but it is asserted that the occurrences of the platinum metals consist chiefly of native metals or alloys of the precious metals containing small amounts of iron, nickel, copper, etc. This judgement is directed by the fact that the precious metals have been frequently discovered in, and obtained commercially from, deposits containing fairly large metallic grains. However, in many deposits, e.g. the sulphide nickel ore of the Sudbury district in Ontario, the bulk of the platinum is too finely dispersed to allow easily the determination of its mineralogical form. It may occur as free metal, as a compound with a non-metal or base metal, or even as a substitute for a base metal in a mineral of the latter. Free metal is suggested as the principal form in the Transvaal sulphide ores. At least some "compounded" platinum is present in the Ontario ores for it was in these that sperrylite was first discovered. It has been recorded that in these deposits, palladium may be present as a selenide. The third type of occurrence, suggested above, may be represented by the Bolivian penroseite studied by Herzenberg (1). This, a complex selenide, was found to contain appreciable amounts of platinum and palladium in addition to the usual base metals. It seems that some information could be obtained concerning these occurrences by an examination of single grains

of the ore constituents. Indeed, such a microscopic investigation was made of the sulphide ore of Norilsk, Russia (2). It revealed three types of grains which were probably precious metals minerals. Of a number of grains isolated, forty-three resembled cuprite but were not identified. Twenty-one appeared to be platinum-palladium alloy, and four were believed to be sperrylite. Obviously, micro-analytical methods applied in these instances would have given pertinent information.

An example of the paucity of information on platinum occurrences is presented by the mineral niggliite. Only one small grain of this has been reported, and the detection of tellurium and a platinum analysis indicated the formula  $PtTe_3$  (3). On the basis of the indexing of the  $x$ -ray diffraction pattern and a comparison of its properties with those of analogous compounds, Meijer preferred the formula  $PtTe$  (4). Although the authors have no information concerning the method of analysis it is a fact that when tellurium is separated as metal, much of the platinum is lost by coprecipitation.

Concerning the mode of appearance of platinum in natural deposits, little has been recorded concerning the possibility of silicate-platinum combinations. Even though it is generally accepted that platinum metals occur almost exclusively in basic and ultra basic rocks, there is some evidence that silicates may be formed. In the authors' researches there have been data accumulated which point almost indisputably to the union of ruthenium or osmium with silica; in the latter case to form residues from which osmium could not be volatilized even at red heat. With ruthenium the incorporation of silica resulted in a residue which resisted the usual treatment and a special technique was required for its separation from the remaining platinum metals. Other researchers have noted the association of ruthenium and silica. Thus Zvyangintsev (5), who provided a more detailed description of his work than one usually encounters, observed silica as a residue subsequent to removal of ruthenium. From these observations it would seem that one should not discount the existence of naturally occurring silicates of the platinum metals.

The principal obstacle in the determination of compositions of these minerals is the difficulty of chemical analysis, especially of minute grains. Only recently have accurate micro analytical methods for individual platinum group metals become available and restricted separation schemes are now appearing in the literature (6, 7, 8).

The minerals of the platinum metals other than those alloys which are composed almost entirely of noble metals, are exceedingly rare. There has been much study of native platinum and a fairly large number of compositions have been recorded. Rather less attention has been given

to iridosmine, the next most important mineral. The older reports of analyses of iridosmine and native platinum are characterized in most cases by an absence of detailed procedure, of reference to inherent analytical difficulties, and of any estimate of accuracy or even precision. The result has been an unreasonable acceptance and perpetuation of unreliable mineral compositions. The difficulties in these analyses are not merely matters of technique; a search of the literature reveals no comprehensive procedure which has been proved valid by either its application to synthetic standards or by the use of some method of comparison. It is partly this situation which introduces a serious element of doubt concerning the meaning and validity of many published compositions of native platinum minerals, particularly of iridosmine. Concerning the latter there seems to have been little appreciation of its identity. Thus, for example, in the analysis of native platinum quoted by Hintze (9), the quantities of the constituents are reported in percentages of platinum, palladium, rhodium, iridium, osmiridium, and some base metals. Osmiridium, or iridosmine is, however, a composite material. Therefore, reports of this kind do not reveal the more significant elementary composition. This neglect would not be particularly significant if the proportions of the iridosmine or "insoluble matter" were very small, but it has been reported present in amounts up to 22.5% in California, 26.0% in Australian, and 37.30% in Oregon platinum. These figures are in contrast to reported iridium contents of only 4.29%, 2.20, and 0.40% respectively.

In view of the above situation, it may be useful to review critically the state of the analytical chemistry of the precious metal minerals and to present a few data on mineral compositions obtained by using a method developed in this laboratory. Since the source of the difficulties in the analysis of platiniferous materials is exemplified in the analysis of iridosmine, this mineral will be considered in some detail.

#### THE IRIDOSMINE SERIES

"Iridosmine" is a name used to denote the members of a series of metallic minerals of the platinum group among which the composition may vary widely. The chief components are iridium, osmium, and ruthenium. Small amounts of base metals as well as the remaining platinum group elements are usually, if not always, present. A considerable quantity of gold has been found in some specimens (10). Originally the investigations of iridosmine resulted in the discoveries of iridium, osmium, and ruthenium and this mineral has remained the principal source of these metals. It was first recognized in the year 1805 (11) and was obtained as a residue upon dissolving crude platinum in aqua regia.

These iridium alloys are frequently very hard, non-malleable, and extremely resistant to chemical attack, especially in the massive state. They are often more resistant than any of the component metals individually, and this property combined with the impracticability of grinding them accounts further for some of the analytical difficulties.

#### DISSOLUTION AND ANALYTICAL METHODS

The first analyses were carried out by Rose (12) and Berzelius (13) but as ruthenium, which is invariably present, had yet to be discovered, the analyses must be regarded as suspect. Subsequent to this work Claus discovered ruthenium (14), and published some analytical data (15).

Of the analyses which are reported in mineralogy treatises, e.g. Dana's (16), the majority were made about one hundred years ago (17). For these, like those of the earlier period, large quantities of fairly finely divided material were used and being in such a form, responded to the attack of a nitrate fusion. Although the older literature is far from explicit, it is to be expected that the dissolution was not complete, for it fails when applied to large grains.

The first major contribution to the special techniques for the analysis of iridosmine resulted from the work of Deville, Debray, and Morin (18). They found that iridosmine could be alloyed directly with zinc, and the latter volatilized leaving the metal in the form of a very finely powdered zinc alloy. Subsequent leaching with acid removed most of the zinc. The resulting powder was largely susceptible to a barium nitrate fusion. This method, intended for the preparation of more than twenty-five kilograms of iridium, was subsequently adapted by Leidé and Quennessen to the analysis of samples weighing about ten grams (19). These authors substituted sodium peroxide for the nitrate in the oxidizing fusion. The mineral, previously pulverized by fusing with zinc, was mixed with 40 g. of sodium peroxide and the mixture added in small portions to 10 g. of molten sodium hydroxide contained in a nickel crucible. The melt was maintained at a bright heat for 30 minutes after which time it was cooled and taken up in a liter of water. Insoluble matter was separated by filtration, washed with sodium hypochlorite, and dissolved in hydrochloric acid.

In order to prevent air oxidation and consequent volatilization of osmium, the zinc fusion was made under a slag, for which alkali chlorides or zinc chloride were used. In a recent publication (20) this oxidation was used to remove most of the osmium which was subsequently condensed. Bearing in mind that there would be only a partial separation of osmium, there would seem to be unnecessary complications.

These zinc and peroxide fusions have become standard procedures for

the attack of iridosmine or the "insolubles" that appear in the course of ore assays. The procedure was accepted by Schubin (21) and Gilchrist (22). Despite its general use the method cannot be considered entirely satisfactory, particularly for the analysis of small samples. Considerable quantities of foreign metals are generally introduced; nickel, iron, gold, or silver from the crucible; sodium or barium from the caustic flux; zinc, and possibly lead and other metals from the alloying fusion. Of even greater concern, is the fact that the attack must be repeated, often several times, to effect dissolution and fails even then to corrode the more resistant alloys. Zvyangintsev (23) indicated what may have been the earlier accepted practice, namely to repeat the caustic fusion until the operator became weary of it and then to discard the still unattacked residue, subtracting its weight from that of the initial sample.

Not only may the process of dissolving be incomplete, but it has been the experience in this laboratory that with certain minerals there may be no evidence of any corrosion. Thus Hill and Beamish were unable to dissolve a sample of Tasmanian iridosmine by these traditional methods (24).

The inefficiency of the classical fusions was recognized by the National Bureau of Standards in Washington. A new approach to the problem was undertaken and led to a much improved procedure (25, 26). By this method platinum metals and their alloys are converted to soluble chlorides by heating to 300° C. in a closed Pyrex tube containing hydrochloric acid and an oxidant such as sodium chlorate. Following the reaction, the tube is opened under a solution of 1:1 hydrochloric acid saturated with sulphur dioxide and appropriate separations and determinations carried out. This method, or modifications of it, is now used by some of the larger platinum metals producers.

In practically all cases attack is complete, but Hill and Beamish found as before that Tasmanian iridosmine resisted quantitative corrosion. It may be that considerable quantities of ruthenium may result in incomplete attack, for this metal exhibits considerable resistance.

In order to ensure complete dissolution of iridosmines Hill and Beamish used chlorine gas at 680–720° C. for the oxidation of micro-samples (24). Although the process is an old one no record exists of its successful application to quantitative work. The alloy must be covered with sodium chloride in order to avoid the formation of an inert clinker in the sample boat. Again, the minute grains of the native alloys were not analyzed by Hill and Beamish, there being available at that time no dependable scheme for the analysis of micro amounts of the platinum metals. However, they found that the chlorination procedure could be used for the quantitative dissolving of iridosmines and was more gen-

erally dependable than the sealed tube method and more convenient in manipulation.

Although the boat residues from chlorinations of iridosmine were entirely soluble and presumably could be analyzed by any valid procedure, there was no justification for assuming that the sublimates and gases that formed could be recovered quantitatively in convenient form, i.e. in aqueous solution, and analyzed. In fact, two major difficulties appeared. Ruthenium and platinum chlorides sublimed and condensed on hot surfaces of the reaction tube to form insoluble crystalline modifications (27, 28); and osmium was difficult to recover, since, in the presence of oxidizing agents, it was converted to the volatile tetroxide. However, as indicated below, these difficulties were overcome.

#### SEPARATION AND DETERMINATION OF THE MINERAL CONSTITUENTS

It is certain that early mineral analyses were carried out on large samples, from which it was relatively easy to recover the constituents quantitatively with, no doubt, some cancellation of errors within the multiplicity of procedures. Unfortunately the records of the compositions of minerals determined by the traditional methods bear no evidence that separations were complete and that isolated constituents were pure. The fact that the totality of the latter was close to one hundred per cent is unacceptable as evidence of accuracy. The device of obtaining the more insoluble platinum metals by difference discourages confidence in the reported values. Where the amount of insoluble was neglected the values are increasingly suspect.

There is then little doubt that some of the early methods of separating the platinum metals were significantly inefficient. Much use was made of ammonium chloride as a precipitant for iridium and platinum. For various reasons this process does not provide acceptable accuracy and at the same time persistently clean separations even upon continued reprecipitation (29). A second procedure used originally, and still so used, for the separation of rhodium and iridium, has been applied analytically. In this method separation is effected by selectively leaching a pyrosulphate melt of the metals, to dissolve rhodium. Such selective dissolutions are seldom if ever to be recommended for precise analytical work. In the past osmium and ruthenium have almost always been separated by distillation from oxidizing media. Although this principle is still accepted as by far the best, the early procedures required improvement.

Apart from the separations, the determinations were not refined until well into the present century. Thus, for example, Leidé and Quenessan (19) collected osmium in sodium hydroxide solution and precipitated it subsequently on aluminium strips. The same authors collected ruthenium

in hydrochloric acid, evaporated to dryness, and after taking up the residue in water, precipitated the ruthenium from solution with magnesium strips. Iridium was also precipitated from the distillation residue by magnesium. Such precipitates were leached with acid to remove the base metal. Thus, it is not surprising that Leidé and Quenessen failed to find platinum, palladium and rhodium in their mineral samples. It is significant that no further samples of iridosmine have been reported free of all of these elements. Osmium was generally determined by distillation into caustic solutions and precipitation by neutralization with acid. This method was shown by Gilchrist to be inaccurate because of the inevitable contamination by alkali (30). Ruthenium distilled and collected in hydrochloric acid was, and often still is, determined by simply evaporating to dryness, reducing the residue in hydrogen, and weighing. Such procedures may suffice for large quantities, but have not proved efficient for milligram amounts.

Because of the general failure to present data in support of procedures, one has the impression that before the Bureau of Standards initiated its program of platinum metals research, the analysis of platiniferous materials depended largely on methods sanctioned only by tradition, few of which had been subjected to critical examination.

In a series of publications, Gilchrist provided schemes of separation and analysis which will probably long remain standard procedures for macro amounts of the platinum metals (31). It was only upon the appearance of these that it became possible to analyze accurately solutions of mixed platinum metals.

However, a great many precious metals assays and associated analyses are concerned with much smaller amounts than those dealt with by Gilchrist. The analysis of small grains of minerals or of the "insoluble" from fire assay methods involves amounts of the order of micrograms.

In the course of twenty-five years of study in the authors' laboratory, micro-procedures for all of the noble metals have been developed. It has been shown that many of the "macro procedures" do not provide accurate results for micro separations and determinations. Micro methods such as the colorimetric, have been appearing for some time but methods of separation are still neglected. Of the latter, some very promising procedures, notably the chromatographic separation of Pt, Pd, Rh, Ir, and base metals (7), have been published, but evidently there has been no integration of these procedures to produce a comprehensive scheme of analysis. Obviously such procedures can not be applied directly to mineral analysis although a number are capable of application to fire-assay buttons or cupellation beads (32, 33, 6, 34, 35).

The authors have also devised a comprehensive scheme of micro

analytical separations for the six platinum elements and have succeeded in developing a procedure for the complete dissolution of platinum metals by the dry chlorination method (8, 36). These publications include verification of the procedures using synthetic solutions and pure metals, and the methods were subsequently applied in the analysis of natural alloys. Some account of this work is included below.

#### ANALYSIS OF MILLIGRAM AMOUNTS OF IRIDOSMINE MINERALS

The difficulties encountered in the dry chlorination of osmium, ruthenium, and platinum, have been overcome. It has been demonstrated that micro amounts of these metals may be converted quantitatively to soluble products and subsequently determined (36). To accomplish quantitative corrosion, the sample was placed in a small Vycor glass tube and covered with sodium chloride. The inside of the tube had to be prepared previously by coating with fused sodium chloride over the regions located at the ends of the hot zone. The tube containing the sample was heated to a temperature of about 700° C., while a slow stream of chlorine was passed through it. The exit gases were led into a train of four receivers containing in the case of the first, sulphurous acid, and thereafter, 6 normal hydrochloric acid, kept saturated with sulphur dioxide by an excess of the gas led into the first receiver. After evaporating the hydrochloric acid solutions to give a few ml. volume, they were combined and analyzed.

The analysis of complex systems follows the course of the analytical scheme published previously (8). The presence of base metals introduces a considerable difficulty. Two approaches to the problem of separation of these may be applied subsequent to the removal of osmium and ruthenium in which process the presence of base metals is not objectionable. The well-known method of Leidé (37) for separating base metal hydroxides from the platinum group is normally quite effective. The separation would be uncertain for small quantities, however, unless a carrier were added to increase the bulk of the hydroxide precipitate. Another disadvantage is the use of nitrous acid which it is desirable to avoid because of the difficulty of destroying the complexes which it forms.

A new approach which promises to be of great value is separation by ion exchange. The principle involves the tendency for base metals to form cations, and the ease of the formation of platinum metals anions. Coburn, et al. (38) have shown that large quantities of iron, copper and nickel may be separated from palladium and platinum by an ion exchange resin. Fraser (39) had thus previously separated small amounts of base metals from palladium. Of the platinum group, palladium is the



most similar to the base metals so it seemed probable that the base metals could equally well be separated from rhodium and iridium using the same conditions. Work now in progress has proved this assumption. The authors have shown in a previous publication that nickel may be separated from iridium (40). Although it was not extensively tested, the following procedure for the removal of base metals was found satisfactory.

The sulphuric acid residue from the distillation of ruthenium was transferred to a 50 ml. beaker and evaporated on a steam bath and a "medium" hot plate to about 1 ml. volume. The sample was diluted with a little water, 5 ml. concentrated hydrochloric acid were added, and the sample was boiled for 0.5 hour, adding more hydrochloric acid when necessary. The sample was boiled finally to 3 ml. volume, 1.5 g. sodium chloride were added and the solution was diluted to about 30 ml. volume. The solution was passed through a column of Dowex 50 ion-exchange resin and the effluent was evaporated to about 20 ml. volume and the separation and determination of palladium, etc. carried out as described previously (8). Most of the sodium was retained by the resin. The column was eluted with 2 normal hydrochloric acid and qualitative tests for iron and nickel applied to the eluates. Iron was precipitated as hydroxide and nickel was detected by means of dimethylglyoxime. These procedures were applied in analyses of iridosmine and other precious metal minerals, and some of the results are recorded in Tables I and II. Samples 1-3 were "iridosmine" of unknown source, No. 4 was a "Tasmanian iridosmine." Samples 5 and 7 were supplied by Harvard University, Department of Mineralogy and labelled "Iridosmine and Osmium" from Colombia. No. 6 was obtained from the American Museum of Natural History and was labelled "Iridosmine form Nizhne Tagilsk, Urals. No. 8 was obtained from the Smithsonian Institution, Washington and was labelled "Iridosmine, var. nevy-anskite, Nevyansk, Urals." An account of the physical examination of these minerals follows:—

Single grains were split or broken into two or more pieces. One of the pieces was examined for the presence of base metals with the aid of a Hilger medium quartz spectrograph with an arc source. Many lines not attributable to the platinum metals appeared in each case, and some of these were identified. In the cases where clear hexagonal habit was not evident, the samples were examined by  $x$ -ray diffraction. The structure of No. 6 was not apparent from microscopic examination but it could not be crushed or ground so that an  $x$ -ray powder pattern was not available. Other pieces of each mineral were analyzed quantitatively. In several cases the grains contained silica in cracks or between lamina.

TABLE I. BASE METAL COMPOSITION OF IRIDOSMINES

No.	Crystal symmetry	Locality	Base metals present
1	} Hexagonal	Unknown	Not examined
2			
3			
4	Hexagonal	Tasmania	Cu, Ag, Pb.
5	Hexagonal	Colombia	Cu, Sn, Pb, Fe*
6	?	Nizhne Tagilsk, Urals	Ag, Sn, Pb, Fe, Cu, Co
7	Cubic	Colombia	Ag, Sn, Pb, Fe*, Cu, Ni*
8	Hexagonal	Nevyansk, Urals	

\* Detected by wet chemical methods.

This was removed by scraping with a needle and in some cases by leaching with hydrofluoric acid. The results of the qualitative examination appear in Table I.

Two parts of the one grain were used in the analyses of Nos. 2 and 3 (Table II). The mineral possessed a lamellar structure, individual plates of which could be split apart with a steel needle. Sample No. 1 was a different grain obtained from the same deposit.

The samples were weighed on a Sartorius micro-balance and were chlorinated for at least 10 hours. Close examination of the solutions obtained upon dissolving the chlorination products failed to reveal the presence of insoluble matter and it was concluded that dissolution was complete. The platinum metals compositions are given in Table II.

Several points of interest are apparent from the investigations. It can be seen that two crystals (samples 1 and 3) from the same locality can differ widely in composition. Fairly good precision was obtained by analysing two portions of the same crystal for ruthenium (samples 2 and 3). This points out the possible lack of significance of existing published data obtained from large composite samples of iridosmine.

TABLE II. ANALYSIS OF IRIDOSMINE SAMPLES

No.*	Weight of sample, mg.	Osmium		Ruthenium		Palladium		Platinum		Rhodium		Iridium	
		µg.	%	µg.	%	µg.	%	µg.	%	µg.	%	µg.	%
1	1.570	600	38.2	5.0	0.32								
2	3.129	1360	43.5	398	12.7								
3	3.924	—	—	475	12.1								
4	0.267	139	52.1	7.0	2.6	3.2	1.2	14	5.3	8.4	3.1		
5	2.921	1210	41.1	442	15.1	13.4	0.5	16	0.6	40.8	1.4	905	31.0
6	1.253	395	31.5	223	17.8	8.5	0.7	47.4	3.8	39.0	3.1	345	27.6
7	1.459	173	11.9	40.5	2.8	8.6	0.6	165	11.3	86.4	5.9	814	65.8
8	1.420	1320	93.0	50.5	3.6	5.2	0.4	10	0.7	8.9	0.6	100.5	7.1

\* The sample numbers correspond to those in Table I.

Hitherto palladium has not been reported as a constituent of iridosmine. Since the procedure for palladium used in the present work is much more sensitive than any hitherto employed, it was possible not only to detect but to determine minute amounts of this metal in the minerals.

Zvyagintsev (41) has suggested that iridium-osmium alloys containing less than 31% osmium possess a face-centred cubic lattice. Sample No. 7 possessed a very low osmium content (11.9%) and *x*-ray diffraction showed it to have a cubic lattice. The lattice cell dimension of iridosmines were reported by Zvyagintsev (5) to vary but slightly with changes in composition and the axial ratio to vary not at all. No marked deviations of the lattice constant from that of pure osmium were observed by the authors among hexagonal iridosmines. Larger differences were observed for the cubic structures but these were still small. This lack of response of the lattice constants to changes in composition is due presumably to the similarity in size of the metallic radii of all six platinum metals.

Thirty-one analyses of Tasmanian iridosmine were reported by Nye (42). Two samples of the Tasmanian mineral were available to the author. Both consisted of very small crystals each weighing about 5 micrograms. By examining the samples under a microscope it was possible to see two and possibly three types of crystals. The most abundant type was the usual tabular hexagonal form; a fairly rare one was long and lathe-like; a third was similar to the nuggets characteristic of native platinum. X-ray diffraction revealed the presence of both hexagonal and cubic modifications.

Several dozen of the hexagonal variety were separated by picking them up with a needle wetted with alcohol. A one-quarter milligram sample was prepared in this way. The osmium value found by the author (52.1%) is higher than the average reported by Nye (*viz.* 45.5%). It is possible that Nye's samples were poorer in osmium due to the presence of cubic (low osmium) constituents, but in view of the variations that can occur among crystals taken from one locality, this explanation may be invalid.

Sample No. 8 was of particular interest. It was in the form of a well defined warped hexagon a little larger than a pin head. A corner of the hexagon was broken off for the analysis and in this process it was observed that the alloy was much more malleable than the other iridosmines and did not "cry" when bent. The bulk of the crystal was placed on a carbon electrode and exposed to the arc for one minute. Unlike all the other minerals examined, it did not melt and yielded only a very faint spectrum from which no evidence of minor constituents was obtained. The crystal was heated to redness in air for a five minute period.

Microscopic examination revealed no apparent change in the crystal other than a darkening of the colour and decrease in the lustre. However, when the crystal was then touched with a needle, it broke very easily and the freshly exposed surfaces were quite black. The osmium probably had been volatilized. Surprisingly the geometric structure was retained upon ignition; it was expected that only a small black residue would remain, considering its high osmium content. Although this sample was labelled "Iridosmine, var. Nevyanskite," it contained more osmium than any sample hitherto reported and more than that allowed by the definition in Dana's System of Mineralogy (16). Actually the amount of osmium present was so great that it was in excess of the optimum amount for the determination. Consequently the total composition reported is somewhat high. It would seem that either the definition should be extended to include minerals possessing a greater osmium content, or else the present sample should be regarded as a native osmium, a mineral category not yet established. In this connection it may be noted that sample No. 7 contained less osmium than any sample previously reported.

In view of the fact that these osmium-iridium alloys may have such varied compositions that two crystal structures are permitted, the designation of all such minerals by the name "iridosmine" seems inadvisable.

It must be emphasized that with milligram samples, results as accurate as those obtainable with macro amounts are not to be expected. Most of the procedures described above are recommended only for micro samples. It is therefore suggested that for maximum accuracy, and where sufficient material is available, a sample of the mineral weighing at least a few tenths of a gram should be started with one of the older procedures and the insoluble material then chlorinated, using the present procedure. The products of the two treatments could be combined, and analyzed by the methods described by Gilchrist.

It should be noted also that in the micro scheme, the determination of iridium is the most difficult of all of the platinum metals determinations. This is partly due to the absence of suitable methods and partly because the determination is made at the conclusion of a long series of difficult operations. It would be highly desirable to have an independent method for the direct determination of iridium, or one which could be applied after the determination of osmium and ruthenium.

#### SUMMARY

Metallic precious metals minerals may be quantitatively attacked by chlorine to obtain salts soluble in aqueous media.

Composite samples of iridosmine should be separated by hand from admixed substances and since such samples are small, they must be analyzed by micro procedures. These procedures are also recommended for the analysis of insoluble material occurring frequently in macro analyses and ore assays.

Analyses of a variety of iridosmine minerals were carried out on the micro scale. It is shown that crystals of iridosmine from the same source can differ widely in composition, but uniformity of composition in a single grain may be expected.

Palladium appears to occur generally in iridosmine in minute amounts.

Since the occurrence of cubic structures in iridium-osmium minerals has been confirmed, the inclusive designation of these minerals by the name "iridosmine" seems inadvisable. The discovery of a mineral containing such a high percentage of osmium that it may well be called "native osmium," also suggests a reconsideration of the nomenclature of the precious metals minerals.

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