Table VI.	Silicon Determination in Calcium Oxide ² with and without Fluoride Treatment

	()	/ silicon per 100 ml.)	
F	With luoride ^b	Without Fluoride	
	$137 \\ 138 \\ 136 $	98 96 91	
Av,	137	95	

^a A 1-gram sample was dissolved in dilute hydrochloric acid, transferred το 100-ml. volumetric flask, and made to volume. Solution was filtered and 2-ml. aliquots were removed for analysis. ^b The 2-ml. aliquots were diluted with water, treated with 0.5 ml. of zirconium-fluoride solution, and warmed for 0.5 hour.

The effect of fluoride treatment is vividly illustrated in Table VI. The results show that a filtered solution may contain unreactive silicon. Conventional recovery experiments may not indicate this type of interference and consequent lack of accuracy.

The problem of loss of silanes during solution of calcium metal was not investigated. It has been reported (1) that slow addition of the metal to dilute sodium hydroxide minimizes the loss of silicon, provided the solutions are kept cool.

METAL. Dissolve a 1-gram sample of metal by slowly adding the fine chips to a Fluorethene beaker containing 15 ml. of about 0.35 M sodium hydroxide. The solution should not be permitted 0.35 M sodium hydroxide. The solution should not be permitted to become warm. After all the metal has been added, acidify the to become warm. After all the metal has been added, acidity the solution by the addition of dilute hydrochloric acid. Add 0.5 ml. of the zirconium-fluoride solution and warm for 0.5 hour at low heat on the hot plate. Complete the analysis, using the recommended procedure.

Weigh the sample into a Fluorethene beaker and dis-Oxide. solve by addition of dilute hydrochloric acid. Add 0.5 ml. of zirconium-fluoride solution and proceed as indicated for metal samples.

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Analytical Chemistry of Niobium and Tantalum

CRITICAL ANALYSIS OF EXISTING METHODS

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A critical review of the main separative reactions employed in the analysis of niobium and tantalum minerals reveals a number of serious defects: the colloidal character of solutions and precipitates, the small chemical differences among the elements, and the large number of repetitive steps involved. It was thought that some of the more serious defects could be overcome by developing nonaqueous separations. For this purpose a new atmospheric chlorination method was developed applicable to the highest oxides of groups IV, V, VI, and VII of the periodic table. The method employs octachloropropane in large excess heated to about 300° C. One conse-

N 1946 there appeared a bulletin (37), which contained a number of comparative analyses on tantalite and niobite minerals of the simpler types, made by different referees using several methods. The tables of data contained in this bulletin admirably illustrate the state of analytical technique with respect to this class of complex substances. Because this bulletin is not as well known in this country as it should be, a few of the results are reproduced here. Table I presents the analyses of two

quence has been the chlorination and distillation separation of titanium and tin from synthetic oxide mixtures containing niobium, tantalum, and related elements. Quantitative removal of titanium and tin from samples as small as 0.1 gram has been effected. With larger samples the niobium(V) oxide may be made spectroscopically free of titanium with one distillation. Zirconium in moderate amounts does not affect the separation. Iron(III) oxide must be removed in advance of chlorination to avoid catalytic decomposition of the chlorinating agent. These separations lay the groundwork for a new system of analysis of the niobite minerals.

different minerals by eight different workers. Four workers used the Schoeller technique (35) and four others used either the Marignac method (21) or modifications of Schoeller's method.

What is very striking about the reported results is the wide variation in analyses for tantala and niobia reported by the four workers who used the same technique—the unmodified Schoeller method (first four columns of data). At the same time, the total percentages of the earth acids are in somewhat better agreement, indicating that in minerals containing little titania the separation of both earth acids from other oxides is more reliable than their

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rame r.	Compa	rative Ana	alyses of	Two Tant	aloniobat	e Ores	
	Schoeller	Method		Modified	Method	Colori- metric	Cunning- ham
Anal, 1	Anal. 2	Anal. 3	Anal. 4	Schoeller	Marignae	Niobium	Method
			Sample I				
$\begin{array}{c} 73.2\\9.48 \end{array}$	$\begin{array}{c} 71.87 \\ 11.2 \end{array}$	$\begin{array}{c} 76.87\\ 16.26 \end{array}$	71.6 9.4	$55.53 \\ 22.73$	$\begin{array}{c} 70.53 \\ 10.41 \end{array}$	$\begin{array}{c} 69.05 \\ 9.15 \end{array}$	$\begin{array}{c} 69.78\\ 12.62 \end{array}$
82.68 2.10 12.6 1.26 1.38	83.07 1.80 13.45 1.77 1.31 0.40 Nil	$83.02 \\ 1.26 \\ 12.93 \\ 15.61 \\ 0.94 \\ \\ 0.36 \\ \\ 0.100 \\ \\ 0.000 \\ \\$	1.4 1.2	78.06 	80.94 1.56 	$78.20 \\ 2.10 \\ 12.10 \\ 1.65 \\ 1.46 \\ 0.19 $	$82.40 \\ 1.83 \\ 13.04 \\ 1.60 \\ 0.94 \\ \cdots \\ 0.16$
			Sample II				
52.0 26.0	$\begin{array}{c} 50.62 \\ 25.53 \end{array}$	$\begin{array}{c} 37.62\\ 40.82 \end{array}$	$\begin{array}{c} 52.9\\ 22.2 \end{array}$	$\begin{array}{c} 42.60\\ 34.84 \end{array}$	$\begin{array}{c} 54.46\\22.73\end{array}$	$\begin{array}{c} 52.76\\ 20.90 \end{array}$	$\begin{array}{c} 52.18\\ 25.66\end{array}$
78.0 3.16 12.5 4.38 2.20	76.15 3.36 12.68 4.57 1.89 0.42 Nil	78.10 1.97 11.89 4.20 1.90 0.36	2.4 2.4 2.2	77.44 	77.19 2.34 	$\begin{array}{c} 73.66\\ 2.94\\ 10.95\\ 4.00\\ 2.16\\ 0.10\\ \end{array}$	77.84 3.26 12.21 4.52 1.76
	Anal. 1 73.2 9.48 82.68 2.10 12.6 1.26 1.38 52.0 26.0 78.0 3.16 12.5 4.38 2.20 	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c } \hline Schoeller Method \\ \hline Anal. 1 & Anal. 2 & Anal. 3 & Anal. 4 \\ \hline & Sample I \\ \hline 73.2 & 71.87 & 76.87 & 71.6 \\ 9.48 & 11.2 & 16.26 & 9.4 \\ \hline 82.68 & 83.07 & 83.02 & \\ 2.10 & 1.80 & 1.26 & 1.4 \\ 12.6 & 13.45 & 12.93 & \\ 1.26 & 1.77 & 15.61 & \\ 1.26 & 1.77 & 15.61 & \\ 1.38 & 1.31 & 0.94 & 1.2 \\ & 0.40 & & \\ & Nil & 0.36 & \\ & & & \\ \hline Sample II \\ \hline 52.0 & 50.62 & 37.62 & 52.9 \\ 26.0 & 25.53 & 40.82 & 22.2 \\ \hline 78.0 & 76.15 & 78.10 & \\ 3.16 & 3.36 & 1.97 & 2.4 \\ 12.5 & 12.68 & 11.89 & \\ 4.38 & 4.57 & 4.20 & 2.4 \\ 2.20 & 1.89 & 1.90 & \\ & 0.42 & & 2.2 \\ & Nil & 0.36 & \\ & & & & \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$

subsequent separation from each other. The unreliability in separation is even more accentuated in the modified procedures. Thus, with sample I, the results reported for tantala vary from 55.5 to 76.7%, while those for niobia range from 9.0 to 22.7%. Similar uncertainties are found with sample II. Large variations are also evident for titania, zirconia, and tungsten. An evident conclusion is that there is a need for improvement in the methods of determining these elements.

The present unsatisfactory state of analysis for these elements may seem particularly surprising, as they were discovered almost a century and a half ago. Two main factors contribute to this situation: the chemical complexity of minerals in which niobium and tantalum are commonly found, and the colloidal character of aqueous solutions of their compounds, further complicated by the presence of elements from the fourth and sixth transition groups. Each of these factors is considered in detail here, in order to analyze probable causes of the failure of current analytical methods, and to indicate the general characteristics which a more suitable analytical approach should have. This discussion will then serve as a guide to the researches which are reported in this series of studies. As a first step it is desirable to examine the composition of the known minerals, in order to assess the magnitude of the problem for which a new solution is sought.

COMPOSITION OF EARTH ACID MINERALS

According to Rankama and Sahama (29) the normal abundance of niobium in igneous rocks is of the order of 20 to 30 parts per million and is about 10 to 20 times that of tantalum. As a result of magmatic differentiation, enrichment of these elements occurs. The best ores and minerals are found in pegmatite dikes and alluvial deposits derived therefrom. From the viewpoint of the analyst they may be divided into simple and complex types.

The simpler types include the niobites and tantalites, (Fe,Mn)O.(Nb,Ta)₂O₅, and the stibio- and bismuthotantalites, (Sb,Bi)₂O₃.(Nb Ta)₂O₅. The term niobite is applied to the niobium-rich members of the isomorphous series; the prefixes mangano, ferro-, stibio-, etc., may be used to denote the preponderance of any associated oxide. As trace constituents-i.e., less than 1% as the oxides-magnesium, lead, nickel, tin, tungsten, titanium, and zirconium are common. Occasionally the tin, tungsten, and titanium percentages are somewhat larger.

The complex minerals include: (a) the rare earth tantaloniobates such as samarskite, yttrotantalite, fergusonite, and microlite; (b) the titanoniobates like aeschynite, euxenite, pyrochlore, and blomstrandite; and (c) those minerals in which the earth acids are lesser constituents while titanium (strüverite, ilmenorutile), zirconium (naegite, hagatalite. eudialvte). or tin (anialite, tantalocassiterite) predominates. In the main these minerals contain significant amounts of the alkalies (sodium, potassium) and alkaline earths (bervllium, magnesium, calcium), along with the rare earths, thorium, uranium (as the dioxide as well as the trioxide), R_2O_3 , silica, and fluorine. The percentages vary so widely among these minerals that instances have been noted where most of the so-called minor constituents listed above were found in a major amount-i.e., in excess of 5%. For a summary of many analyses on these types of minerals the reader is advised to consult Schoeller's magnificent book (35).

A consequence of this degree of complexity is that a large number of separation reactions and separation steps are required in order to divide a sample into its component parts. This leads to the development of large cumulative errors merely from the handling operations without regard for the chemical problem which, with respect to its complexity, represents the analyst's Pandora's box.

THE PROBLEM OF CHEMICAL SEPARATION

Unlike most metals, niobium and tantalum in aqueous solutions do not form simple water-soluble ions. In neutral or even weakly acid solutions their compounds are hydrolyzed to give hydrated oxides of uncertain composition possessing great adsorptive properties. To a lesser degree titanium, zirconium, and tin possess similar properties. To obtain water-soluble compounds it is necessary to work with complexes of the polyhydroxy acids or the complex fluo acids. In these complexes, the three main elements-i.e., niobium, tantalum, and titanium-show little dissimilarity and, therefore, separation techniques tend toward successive fractionations rather than clear-cut separations.

To compound the complexities of this problem, known analytical reactions for the precipitation of these elements and zirconium differ in mixtures from those observed with solutions of the individual elements (12, 24). This is probably due to the formation of isomorphous mixtures not only in flocculated precipitates but also in the colloidal solution parts. Schoeller describes this situation as follows:

Each individual constituent, more particularly a subordinate one, cannot behave quantitatively toward reagents as it would in the pure state because its molecules are too firmly interlocked with those of another constituent of different chemical reactivity. Thus, a mixed earth-acid precipitate containing more tantalic than niobic acid reacts like tantalic acid. If the reverse is the case, the mixture behaves like niobic acid; with this difference, that a higher proportion of niobic acid is required to mask the presence of tantalum. This applies also to complex precipitates containing tantalic and titanic acids, while niobic and titanic acids in admixture mask each other more completely than do tantalic and titanic acids,.... the precipitates obtained in the analysis of minerals by the usual hydrolysis method were even more intractable, as they contain several minor constituents in addition to the three principal ones mentioned. Thus stannic and tungstic oxides are generally present, and their extraction from the hydrolysis precipitate by means of ammonia and ammonium sulphide (sic) is incomplete. Again, zirconia strongly modifies the normal behavior of titania (and vice versa) in mixtures of the two oxides; it also affects that of the earth acids, especially if titania is present as well. The above considerations on complex precipitates are of great

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importance, as they assign a common cause to most of the difficulties and complications of earth-acid analysis.

As a consequence of these conditions, the notable advances in the analytical chemistry of these elements have been associated with the discovery or development of reactions which in the main were concerned with separations of definite stoichiometric compounds of these elements.

The early research on niobium and tantalum following their discovery by Hatchett (10) and Eckeberg (7), respectively, was largely confined to attempts to establish conclusively that these were indeed two different elements. The principal investigators of this problem were some of the most celebrated scientists of their time. They included Wollaston (45), Berzelius (3), Wöhler (44), Rose (30), Hermann (11), and Marignac (21).

Not until Marignac (21) characterized the composition of the complex fluo salts of these elements could their individuality even be definitely established. Taking advantage of the low solubility of potassium fluotantalate, he effected a separation of that element from niobium and was thus able to analyze a number of their minerals. He was not able, however, to separate titanium by means of the fluo salts (22), because its solubility was intermediate to those of niobium and tantalum.

As the solubility of $K_2 TaF_7$ is about 0.66 gram per 100 ml. of water, while that of $K_2 NbOF_3$, H_2O (the niobium salt formed under comparable conditions) is about twelve times more (23), it can be seen that the separation of the fluotitanate with an intermediate solubility would be difficult to achieve analytically.

It was Schoeller and associates (35) who finally devised a complete separative scheme during a 17-year period commencing in 1920. Most of these researches are described in the *Analyst*. The principal contribution of Schoeller resides in his discovery of a number of reactions in which the earth acids and their associated elements can be precipitated from media in which they are soluble.

One of these reactions involved the formation of soluble, moderately stable oxalate and tartrate complexes. It provided a method for bringing the earth acids and associated elements into solution after pyrosulfate fusion of the mineral. From this solution after separation of an insoluble residue (usually small, which results from inadequacies of the pyrosulfate fusion and contains silica, cassiterite, and lead sulfate) the hydrogen sulfide group may be removed. After this, hydrolysis of the tartrate complexes of the earth acids in hydrochloric acid solution results in their precipitation along with tungstic oxide. Except in small quantities titanium and zirconium would interfere. Thoria and uranic oxide precipitated at this point only in trace quantities. Thus this method, when applied to minerals free of titanium and zirconium, provided a separation from aluminum, beryllium, the rare earths, iron, and manganese. Tungsten may be separated as tungstate by precipitation of the 4Na₂O.3Ta₂O₅ and 7Na₂O. 6Nb₂O₅ salts from a solution of the potassium salts by saturation with sodium chloride.

The second important reaction discovered was the great difference in stability between the titanium salicylate complex and those of the earth acids. When an oxalate solution of these three oxides was treated with sodium salicylate, an orange color developed due to the titanium complex. Addition of calcium chloride at this point resulted in a precipitation of calcium oxalate and the earth acids. The titanium remained in solution as the orange complex. While this separation was not complete and reworking of the titania fraction was necessary, it nevertheless constituted one of the best separative procedures developed.

A third important development lay in the reinvestigation (following Rose, 30) of tannin as a reagent for the precipitation of the earth acids from a weakly acid or neutral oxalate or tartrate solution. Because the niobium precipitate is red and the tantalum is sulfur-yellow and because the precipitation is stepwise in character, the two can be separated in a fractionating procedure seldom requiring more than three complete cycles of ignition, fusion, leaching, and precipitation for complete separation. These reactions in addition to a group of minor ones constitute the basis for the Schoeller analytical schemes.

From a detailed review of these schemes it becomes evident that even the simplest will probably be much more complex than anything the average analyst may have previously been called upon to do. Separations are not clean cut, but require repeated reworking of filtrates and precipitates. This results in a complexity which raises the probability of personal error enormously. More than that, the handling of half a dozen precipitates or more at a given stage necessarily results in a magnification of indeterminate losses. Finally, heavy reliance is placed on the judgment of the individual analyst, who must frequently decide without clear-cut evidence whether the niobium-tantalum separation is complete or whether a certain modification must be introduced, etc. Consequently, an excessively high degree of analytical skill is demanded of the operator. In addition, about 12 to 15 days of painstaking labor are usually required to achieve a complete analysis.

Serious attempts have been made to modify the original Schoeller method in order to reduce the time necessary for an analysis, as well as to improve its reliability. These attempts, in the main, either concentrated on substituting other methods for the tannin separation of niobium and tantalum, or attempted to rearrange the entire scheme in the interest of economy of operations. The modifications proposed for earth-acid separation include:

Attempts to reduce the niobium to the trivalent state, thus permitting its oxidimetric titration in the presence of tantalum (5, 6, 16, 17, 25, 36, 41, 43). This would allow an analysis of such mixtures, the tantalum being determined by difference. Schoeller and Waterhouse (34) have criticized this method adversely. Knowles and Lundell (19), however, have empirically found the proper conditions for quantitative reduction, so that this approach is now possible. Nevertheless, the prospects of this analysis are not alluring because of the exacting and laborious reduction technique. Titanium must be absent or suitably corrected for.

Development of colorimetric methods for the determination of niobium or tantalum or both. One such group is based on the yellow color of the peroxy complex of niobium (8, 18, 40) formed in concentrated sulfuric acid. Suitable corrections must be made for any titanium, tungsten, rhenium, molybdenum, etc., which may be present. Tantalum is determined by difference. Platonow and colleagues (26, 27) studied the reactions of niobium and tantalum with various polyphenols. They observed that tantalum gives a yellow color with pyrogallol only in acid solution, while niobium reacts to form a somewhat similar yellow color only in alkaline solution. This reaction has been incorporated into methods of analysis developed by a number of other workers (1, 42), where it is applied to the determination of niobium in the tantalum fraction and to the determination of tantalum in the niobium fraction of the tannin precipitates. Such an approach eliminates much of the tediousness of that separation. It suffers from the interference of titanium, iron, etc., and also from the errors introduced in the many preceding separative steps.

In an effort to reduce the time required for analysis of Brazilian tantaloni
obates, Slavin and Pinto $(\mathcal{37})$ developed a rearranged Schoeller procedure which reduced their operations to 5 days. Their innovation consisted of a separation of the bulk of the titanium, iron, manganese, the alkalies, and rare earths by hydrolyzing the pyrosulfate melt in a 2.5 M hydrochloric acid solution. To ensure complete precipitation of the earth oxides which would be solubilized by the titanium, tannin is added. If this operation is repeated, about 85% of the titanium is separated in two stages, leaving the separation of the earth oxides as the main analytical problem. This was indeed an important development for the analysis of the simpler minerals. In the opinion of these authors (37, page 50) it constituted an extraction "of the last possibilities out of the Schoeller method." They also thought that "any significant improvement will require a radical change, either in the volumetric methods or else an entirely new approach.' With this conclusion there can be little disagreement.

This review and description of the Schoeller approach and all subsequent modifications of his approach to the analysis of simple and complex minerals containing the earth oxides are made in this brief form to lay a basis for the fundamental conclusions:

1. The analytical separative schemes of this approach do not give quantitative results without repeated precipitations and reworking of these precipitates. To achieve reasonable precision, therefore, requires long periods of time and many tedious and repetitive operations.

2. From the standpoint of the reactions themselves, it is clear that at almost every stage of the analysis there is either a colloidal solution or a colloidal precipitate to contend with and almost never solutions or precipitates involving simple ions or compounds. It is this condition which is responsible for the complexity of these analytical schemes.

3. Schoeller correctly diagnosed the main reason for the difficulties which had defeated the efforts of earlier workers (except Marignac). Nevertheless, the reactions that he developed were subject to the same difficulties. Although he often started with complexes in true solution, hydrolysis was unavoidable in his scheme of operation, and the resulting precipitates were invariably colloidal in character. As such, adsorption was inevitable, as was "loss of chemical identity." In his massive and painstaking investigations, this master analyst extracted most of the potentialities of these complicated aqueous reactions. It therefore appears more profitable to seek an alternative approach, perhaps more difficult to develop in the preliminary stages, but basically simpler in the separation of the earth acids. To this end the basic inorganic chemistry of the various elements was considered in a search for a class of compounds, simple in character and suitable for clean-cut separative reactions. The choice of compounds finally narrowed down to the anhydrous chlorides, where for reasons of ease of preparation, and a combination of suitable physical and chemical properties, a start was made. In the next section some of the reasons underlying this choice are developed.

The essential difference of the approach described is that the main separations are made in nonaqueous systems where the difficulties of working with colloidal systems are excluded. While this initially poses many new difficulties it meets a requirement which all satisfactory analytical methods fulfill—i.e., handling compounds of simple and definite stoichiometry. This approach has already resulted in a method for the separation of titanium from the earth acids, so complete and satisfactory that in only one operation the concentration has been reduced beyond spectroscopic detection. This operation, involving an element intermediate in its chemical behavior to the two earth acids, is basic to the further development of their separative reactions. Its solution, therefore, confirms in a minor way the validity of the approach suggested above and allows a direct attack on the separation of niobium from tantalum.

(Analytical Chemistry of Niobium and Tantalum) CHLORINATION OF OXIDES AND THOSE OF RELATED ELEMENTS

THIS paper reports a number of qualitative and a few quantitative investigations concerned with the atmospheric chlorination of oxides likely to be found in tantalite and niobite minerals. The decision to make this investigation developed from a review of current analytical methods for such minerals, from which it became evident that a nonaqueous approach was necessary if cleancut separations were to be achieved. The anhydrous chlorides were selected for the contemplated analytical scheme as a result of several additional considerations.

An examination of the boiling points of the elements of groups IV, V, and VI blocked out in Table II (28) shows a real possibility for separations involving a low boiling and a high boiling group.

This would mean the separation of titanium, tin, silicon, germanium, vanadium, arsenic, antimony, and hexavalent uranium from niobium, tantalum, zirconium, and tungsten. The 100° difference in boiling points which exists between the titanium and the niobium and tantalum thus appears as an obvious chemical difference to exploit.

In the second place, a separation of titanium from niobium and tantalum was considered a most desirable first step, as it results in a considerable simplification of complete analytical schemes for these minerals (26, 37). Thus it seemed best to develop first the chlorination reaction and then the distillation

separation of titanium.

Recent studies of reactions for the preparation of the anhydrous chlorides of niobium and tantalum (4, 13, 31, 32, 38, 39) have used either carbon tetrachloride or carbon and chlorine as the reagents. The oxides were chlorinated generally in the 200° to 350° temperature range, using a sealed and evacuated bomb tube as the reaction vessel. Success with niobite ores was also reported. On the other hand, attempts at chlorinating niobic oxide at atmospheric pressure led to almost quantitative yields of the oxychloride, NbOCl₃. Titanic and tantalic oxides could not be chlorinated in such a system. Hall (θ) obtained similar results with sulfur monochloride.

The requirement of a sealed high pressure chlorinating apparatus excludes the development of an easy distillation technique. To open the bomb tube and transfer the contents quantitatively to a distillation apparatus without hydrolyzing the reactive chlorides is difficult and time-consuming. It was necessary therefore to develop a chlorination technique operable at atmospheric pressures and thus convenient for use in the boiler of a still.

MATERIALS AND REAGENTS

Niobium(V) Oxide. This was the high purity grade niobium oxide sold by the Fansteel Metallurgical Corp., North Chicago, Ill. The principal impurities are 0.2% Ta₂O₅, 0.002% TiO₂, 0.001% Fe, and 0.03% SiO₂. This reagent was used without further purification, except for ignition to remove water vapor or volatile constituents absorbed on it.

Tantalum(V) Oxide. This is the Type 400 grade obtained from the Fansteel Corp. It is made more reactive by being given a pyrosulfate fusion followed by leaching into dilute ammonium hydroxide. The precipitate is filtered and then washed with successive portions of ammonium hydroxide, followed by ignition to constant weight.

The titanium(IV) oxide and other oxides were c.p. analyzed chemicals used without further purification.

Group IV SiCl ₄ 57°		Group V		Group VI		
TiCl ₄ 136	GeCl₄ 84	VCl4 164	AsCla 122		SeCl4 Unstable	
ZrCl4 331	$_{113}^{ m SnCl_4}$	NbCl₅ 243	${}^{ m SbCl_{5}\ (172)}_{ m SbCl_{8}\ (219)}$	MoCls 268	${ m TeCl_4}$	
HfCl4 317	PbCl ₄ decomp.	TaCl₅ 234	BiCl: 441	WCl ₆ (337) WCl ₅ (276)	${ m TeCl_4}$	
ThCl4	to PbCl ₂			UCls (sublm. 50° C.)		
922 FeCls 319			UCl4 (very high)			