TANTALUM PRODUCERS INTERNATIONAL STUDY CENTER

QUARTERLY BULLETIN ISSUE No 25 MARCH 1981 FIRST QUARTER

T.I.C. Activities

A two-day meeting including the Fifteenth General Assembly of the T.I.C. will be held in Bad Harzburg and Goslar, West Germany, on May 19th and 20th 1981. The formal business meeting and seminar will be held in the Hotel Intermar in Bad Harzburg. A plant visit will be made to the Goslar plant of Hermann C. Starck Berlin, the company which will very kindly act as host to the T.I.C. on this occasion.

The programme for the meeting is as follows :

Monday, May 18th — Hotel Intermar, Bad Harzburg
- Arrival of delegates and guests in Bad Harzburg
- Early evening welcoming cocktail party

Tuesday, May 19th — Hotel Intermar, Bad Harzburg
- At 9 a.m. the General Assembly will begin, open only to delegates of member companies
- After a short break, when other delegates and guests will join the meeting, there will be a seminar focusing on the end-use of tantalum products. It is expected that the papers to be presented will cover applications of various products, expected changes in markets for these which will affect tantalum consumption, and forecasts of future trends in these markets.
  Speakers will include :
  Mr William F. Mooy
  Commodity Group Manager, Hewlett Packard;
  Mr Eric Ossman
  Vice President and General Manager, Siemens Corporation;
  Mr Hidehiro Okuda
  General Manager, Nippon Electric Co. Ltd.
- This will be followed by a panel discussion on the potential of the People's Republic of China as an exporter of tantalum materials and products and a customer of Western tantalum producers and processors.
- In the evening all participants will be the guests of Hermann C. Starck Berlin at a banquet dinner in the Kaiserpfalz, Goslar. The guest speaker will be Dr Engelmann of the Ministry of the Economy in Bonn.

Wednesday, May 20th — Goslar
- Transport will be provided from Bad Harzburg to Goslar for a conducted tour of the processing plant of Hermann C. Starck Berlin
- Afternoon free in Goslar.

Although the seminar and general discussions will be open to all delegates and invited guests, we regret that participants from other processing companies can not be included in the plant visit; they will already be familiar with the work involved.

A touring programme will be arranged for ladies in the party, visiting the Harz Mountains on Tuesday and the town of Goslar on Wednesday morning.

A number of rooms has been reserved at the Hotel Intermar in Bad Harzburg for the accommodation of the participants. The nearest airport is at Hannover, about eighty kilometres away.

Invitations are being sent to the representatives of all member companies by the Secretary of the T.I.C., from whom further information concerning the meeting may be obtained.

T.I.C. FIFTEENTH GENERAL ASSEMBLY

The Fifteenth General Assembly of the T.I.C. will be held as part of a meeting from May 18th to 20th 1981 in Goslar and Bad Harzburg, West Germany, hosted by Hermann C. Starck Berlin.

The General Assembly will be convened at 9 a.m. on Tuesday, May 19th, in the Hotel Intermar in Bad Harzburg. The Agenda for the meeting will be :

1. **Presidential Address by Dr George J. Korinek.**
2. **Minutes of the Fourteenth General Assembly.**
3. **New membership.**
4. **Report of Executive Committee.**
5. **Report on quarterly Bulletin.**
6. **Accounts for 1980.**
7. **Budget for 1981.**
8. **(a) Production statistics for 1980;**
   (b) Proposed reporting of processing statistics.
9. **Statutory elections.**
10. **Sixteenth General Assembly : place, date.**
11. **Other business.**

The formal business of the association will be followed by a series of presentations covering the end-use markets for products containing tantalum. There will also be a round-table discussion of the potential of the People's Republic of China both as a supplier of tantalum materials and as a consumer of tantalum products.

On Wednesday, a visit will be made to the Goslar plant of Hermann C. Starck Berlin, a major producer of tantalum and niobium products as well as a principal processor of tungsten, molybdenum and other special metals and chemicals.

The Harz Mountains area of West Germany

The Harz Mountains are the most northerly mountain system of Germany and are situated between the Weser and Elbe rivers. They extend in a northwest to southeast direction from the area south of Hannover in West Germany toward Leipzig in East Germany. The Harz is a mass of Palaeozoic rock rising through the Mesozoic strata of north Germany and is bounded on all sides by faults. Slates, schists, quartzites and limestones form the greater part but some peaks are intrusive granite. Metalliferous veins are common.

Mining has been carried out since the tenth century. The principal mineral mined during the centuries has been rich argentiferous lead, but gold in small quantities, copper, iron, sulphur, alum and arsenic are found. Marble, granite and gypsum are also worked. The richness of mineral deposits brought fame and wealth to the area. The silver attracted emperors and dukes. From the eleventh century until the thirteenth, a principal seat of the Holy Roman Emperors was located here.

The summer is usually pleasant on the hilltops and in the valleys of the Harz, although the climate is often cold and damp in the winter. With fine weather added to the scenery, forests and legendary and romantic associations, the Harz is a favourite summer resort.

Bad Harzburg is situated on the northern slope of the Harz Mountains only a few kilometres from the border between the two Germanies. As its name suggests, the town is a spa and possesses brine and carbonated springs. There are several comfortable resort hotels and a casino.

Goslar, the location of the Hermann C. Starck Berlin plant, is about ten kilometres west of Bad Harzburg and is really the gateway to the Harz Mountains from the west. Goslar was founded in 922 A.D. by Henry I. It has had a long history as a seat of dukes and emperors and an imperial palace is located here, built in 1010 by Henry II. In this role and later as a free town, Goslar has contributed much to the history of Germany.

Goslar is a charming town of medieval streets lined with half-timbered houses, romanesque and gothic churches, palaces, guild halls and parks. Because of its wealth, Goslar has always been an attraction and in the middle ages was frequently attacked. To ward off the foes, the defences of the town were built and improved from year to year. Around 1500 A.D., Goslar was protected by fifty fortified towers. But since that time the ramparts have been turned into gardens and parks, with an enjoyable walk leading around the town following the former wall. Sections can still be seen and some of the remaining massive towers are used today as residences, offices and museums.

Goslar is a beautiful town with many attractions. Delegates and guests to the T.I.C. meeting should plan some extra time to enjoy it and the neighbouring mountain area.

Hermann C. Starck Berlin

The host for the Fifteenth General Assembly will be Hermann C. Starck Berlin, which was established about fifty years ago and has grown to be one of the world's leading special metal processors. In addition to the large plant in Goslar, Starck has a metallurgical processing plant at Laufenburg/Baden near the German-Swiss border.

The Starck plants comprise a very versatile combination of mineral dressing, chemical processing, and pyrometallurgical operations. This variety of available installations, coupled with an extensive capability developed over the years, gives Starck an unusual flexibility in treating almost all types of raw materials in the special metals area. Both plants have modern laboratories equipped with every type of testing and quality evaluating instrument to ensure that products satisfy the most exacting specifications.

Although Starck is Europe's leading producer of tungsten and molybdenum products, its product line covers almost all forms of metals and chemicals derived from cobalt, nickel, tantalum and niobium. Starck is probably best known for the broad line of carbides produced for the cemented carbide industry. But, in addition, it manufactures nitrides, silicides, borides, pure powders and other compounds of the special metals for a great variety of applications as well as a full line of special alloys produced both by pyrometallurgy and powder metallurgy.

In the niobium and tantalum processing area, the plant at Goslar is fully integrated from ore and concentrate processing to finished products. The basic operation is the chemical dissolution of the ore followed by liquid-liquid extraction resulting in refined oxides and potassium-tantalum fluoride. Further processing results in the world's largest single plant output of carbides. By a proprietary reduction process Starck also produces capacitor-grade tantalum powder. Starck first introduced the high-rated capacitor powders at levels of 12,000 CV/gram.

Over the years Starck has emphasized strong research and development in well equipped laboratories. The excellent facilities at Goslar provide these. The Starck stated philosophy is to research actively all aspects of the tantalum and niobium businesses and to concentrate on the production of the most important products without neglecting the side-lines.

Tantalum and niobium jewellery

Tantalum, niobium and titanium are now being used by designers to make beautiful pieces of jewellery: earrings, brooches and necklaces. The designers find that the permanent intense colours which can be obtained by anodizing provide real beauty in the jewellery made from these otherwise nondescript metals. Although titanium is the lightest of the three metals, it is very tough and allows only limited shaping. Thus niobium and tantalum, being very workable, are preferred. The weight of tantalum is not a disadvantage as the density compares directly to that of eighteen carat gold, and wearers of jewellery are accustomed to this weight.

Since no dyes or pigments are used, the colours obtained by anodic oxidation are permanent and the pieces can be worn in sensitive areas, such as ear lobes, without any allergic reaction. The oxide layer is very hard, thin and transparent. The intense colours result from optical interference which produces iridescent effects. A complete spectrum of colours ranging from blues and greens to pinks, purple and gold can be obtained, reminiscent of butterfly wings, soap bubbles and peacock feathers. The thickness of the oxide film determines the colour which will be obtained. To vary the thickness, the time of heat application or the rate of this determines the amount of oxide which will build up. Although the oxide layer can be generated by the direct application of heat from a torch, electric anodization is preferred because of the ability to effect better control and more subtle gradations of colour.

To obtain the colouring effect, several techniques are used. The most controllable method is total immersion of the piece to be coloured in an electrolyte bath. The piece of jewellery is attached to the anode and suspended in an electrolyte solution. A high voltage source is applied to a cathode in the cell and to the anode. The variations in colour are obtained by variation in the voltage applied and by the length of time of application. The results are toward browns at low levels of applied voltage through yellows, greens, blues to pinks as the voltage is increased. A variation of this method can be used to obtain gradations of colours or a spectrum effect by attaching the anode to a plastic rod which permits changing the depth of immersion during the anodizing process.

An alternative method is to place the piece of jewellery on a flat metal plate which serves as the anode. By then attaching the cathode wire to the metal ferrule of a water-colour brush and using an electrolyte solution, it can be used to « paint » on the piece. Again, variation in applied voltage and time are the factors which determine the colours.

Which ever method is used, the results provide an entirely new dimension in jewellery design unobtainable by any other method. Although colouring can be obtained by painting, enamelling, etc., no other method provides the beautiful iridescence and pureness of colour. Flowers, birds, gem shapes, in combination with silver and gold settings, have resulted in a beautiful assortment of very attractive pieces of jewellery. The more expensive pieces, some known to have ranged to prices of a few thousand pounds, are often set with gem stones, particularly brilliants which pick up the beautiful colours from the metal.

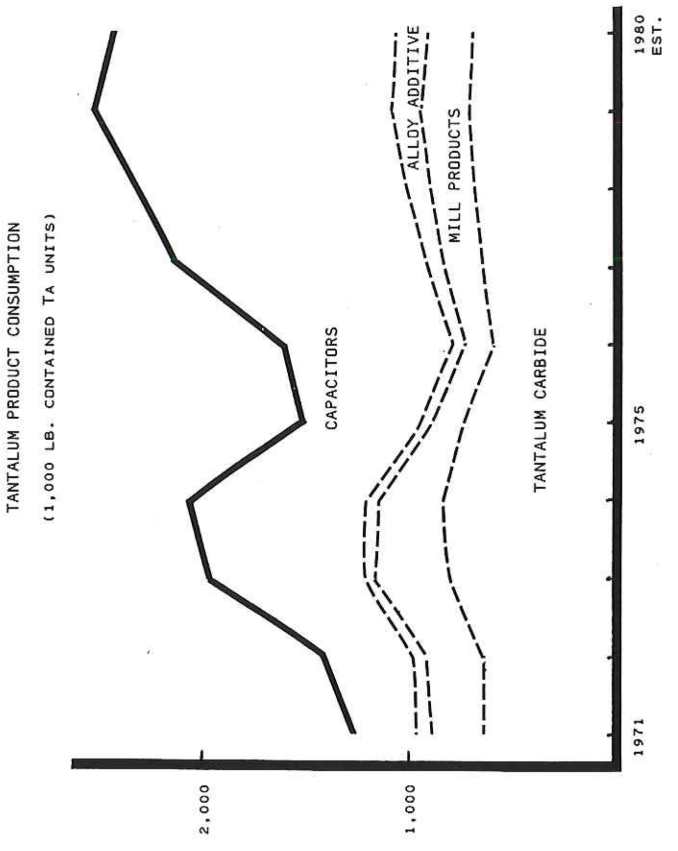
This old technology of anodization applied to a new product was first developed in the United Kingdom a few years ago by designers experimenting with the use of other metals in place of the conventional silver, gold and platinum. As a result, the focal point of this new art is in England and many pieces can be found in the shops of London. Several very accomplished designers are producing many original pieces which have been displayed in exhibitions in the U.K., Belgium, Australia and the United States. So much interest has been generated among designers that the techniques have spread and workshops are now being offered for professional jewellers in several locations in the United States.

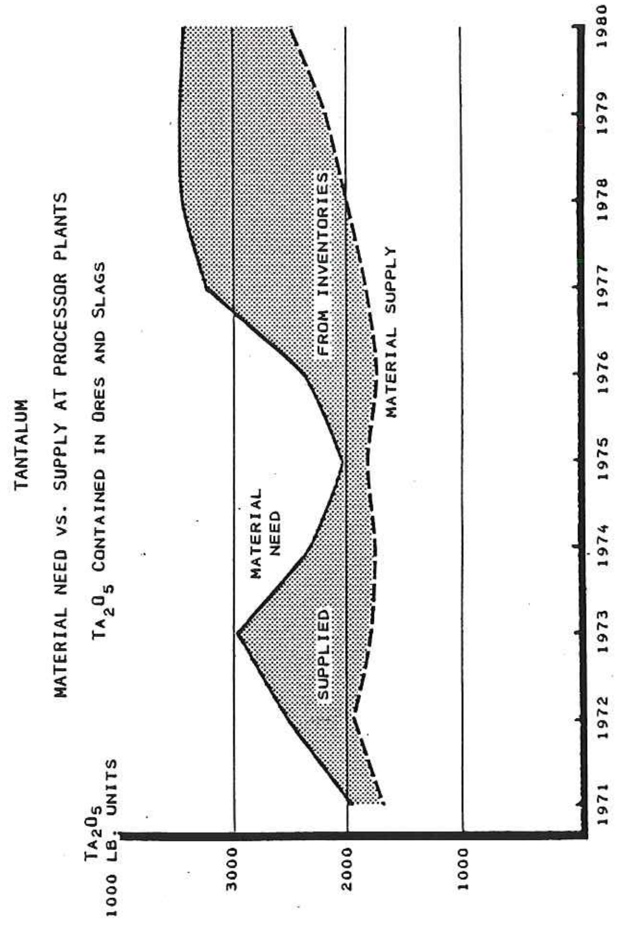
A decade of growth : Tantalum

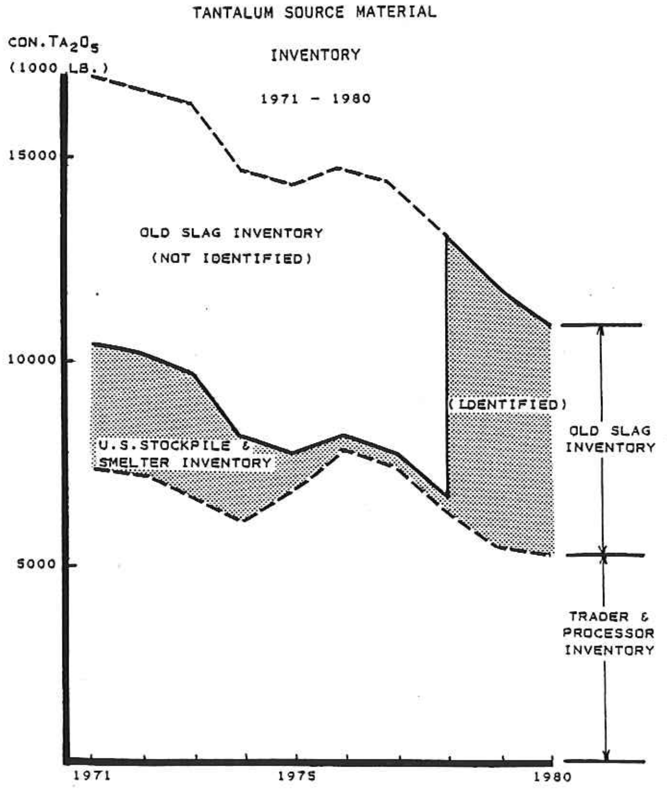
The period from 1971 through 1980 has been a decade in which the tantalum business has matured and tantalum has become firmly established as a commercial commodity. Whereas, prior to 1971, the market for tantalum had been dominated by use in military and aerospace hardware, at the end of the decade tantalum is being principally consumed in commercial applications with only a very small portion being used in the applications of the 1960 decade. But the decade has also been characterized by an insufficient supply of tantalum materials from currently producing sources to meet the growing market needs. Only inventories of tantalites and tin slags produced prior to 1971 have made it possible to support the growing need.

THE TANTALUM MARKET

During the decade, the consumption of tantalum products has almost doubled with an overall average annual growth rate of $7\frac{1}{2}$ %. But the shift in the market is evident when the consumption is broken down by the four principal product groups :







Whereas in 1971 tantalum carbide use was 50 % of the total consumption, in the 1979-1980 period capacitor products had reached 56 % of the market. The tremendous growth of the tantalum capacitor market resulted in an average annual growth rate of $17\frac{1}{2}$ % in the tantalum products consumed. Thus by 1980 over four times as much tantalum was being consumed in capacitors than in 1971. The carbide and mill product markets have shown no growth. In these areas efforts to recycle, conserve and substitute have been quite successful. Although the use of tantalum as an alloying element in high-temperature alloys has grown at the rate of $10\frac{1}{2}$ % per year, this use in 1980 amounted to only 6 % of the total tantalum consumption.

When this demand for product is converted into a demand for tantalum source materials, there has been a growth from about 1.75 million pounds contained Ta_2O_5 in 1971 to almost 3.5 million pounds in 1979.

TANTALUM SUPPLY

There has been an increase of 30 % in the supply of tantalum from current sources from 1970 to 1980. This increase has developed entirely in the past two years, inspired by high prices. There has been a major change, however, in the use of source materials. In 1971 almost the entire production of tantalum came from tantalites and high-ratio columbites. But by 1980, over one-half of the source material used was tin slags, lower-ratio columbites and struverites.

USE OF INVENTORY

The shortage of material from current producing sources is evident from a direct comparison with need when lead-time adjustments are made to look at demand and supply as seen by the processor (see graph).

The gap has had to be made up from inventories, material produced in excess of need prior to 1971. By 1971, due to continuing tin production for decades, unwanted piles of tin slags containing tantalum had built up. In addition, in 1973 the U.S. Government revised the National Stockpile objectives and made ores and concentrates available to the market. As a result, 30 % of the material consumed came from these old supplies. A summary of consumption from 1971 through 1980 clearly shows the advantage of these accumulations :

	Million lb. *Ta_2O_5*	%
Total need by processors :	27.8	100
Total supply to meet the need :		
— From current producing sources	19.4	70
— From tin slag inventories	5.3	19
— From U.S. Stockpile	1.1	4
Total	25.8	93
— From processors' inventories	2.0	7
Total material processed	27.8	100

These inventories available for use were tremendous. In 1971 the total was almost 20 million lb. Ta_2O_5 even though a lot of the material had not even been identified at that time. At the end of 1980, the inventory is still the equivalent of 10 million lb. Ta_2O_5 in ores and concentrates after allowance has been made for the loss in upgrading the slags.

However, most of the better grade slags have been used and about 25 % of the remainder is in very low-grade slag containing less than 2 % Ta_2O_5. Fortunately, the technology for upgrading very low-grade slags has been developed during the decade and the use of all of this material is only a matter of economics.

It is also evident that producers have responded to the increase in demand. Unfortunately, the time required to expand source of supply prevents a rapid change and so adequate supply has lagged behind demand by three to four years.

MATERIAL PRICES

The decade has also seen a dramatic change in tantalum prices, the great increases resulting from the rapid escalation of demand. Processors, having to obtain material to meet their customers' demands, have been very competitive in buying materials. Whereas 30 % tantalite could be purchased for U.S. $ 5 in 1971, it reached U.S. $ 115 to $ 125 in 1979. Even the low grade slags which could not be sold at all in 1971 reached prices ranging from U.S. $ 25 for 1.5 % material to U.S. $ 60 for 5 % material.

The basis of these price increases is evident when considered on a year to year basis :

Year	*Ratio to current need* *Change in T&P* Inv.*	*Total T&P Inv.*	*Back-up Inv.*	*% change in average price (MB)*
1971	− 11 %	4.0	1.9	—
1972	− 25 %	3.1	1.3	+ 15 %
1973	− 21 %	2.4	1.1	+ 30 %
1974	+ 33 %	2.4	.9	+ 80 %
1975	+ 41 %	3.1	.4	— 15 %
1976	− 15 %	3.0	.2	+ 18 %
1977	− 39 %	2.4	.1	+ 26 %
1978	− 24 %	1.8	.1	+ 200 %
1979	− 4 %	1.5	1.8	+ 90 %
1980	+ 8 %	1.6	1.6	+ 20 %

* Traders' and Processors' Inventory.

Although prices began to rise rapidly in 1973 and 1974, the 1975 recession causing a 25 % drop in demand resulted in surplus supply providing processors with the opportunity to rebuild their inventories. But the rapid upturn in the market in 1976 again forced reduction in inventories with the beginning of another upward trend in the price of materials. The combination of reduced processor inventories and the apparent exhaustion of back-up supplies from the U.S. Stockpile and available slag inventories at smelters caused an acceleration in the price increase in 1978 and 1979. It should be noted that most processors were unaware before 1979 of the actual usability of the very old tin slags excavated and made available beginning in 1978. In 1980, however, recessionary effects and confidence in adequate supply have levelled the material price and even resulted in a small reduction for some materials.

LOOKING FORWARD

It is a general opinion that the demand will stay level for the next few years. Adequate supply is assured as expansion of currently producing sources will carry on and the doubling of slag-upgrading facilities will provide the needed additional material required to effect demand/supply balance. The potential of materials from China plus new source developments in Zaire, Australia and Egypt assures continued supply to meet market needs.

The analytical chemistry of tantalum

The following article was provided by Dr. Roland Young, Consulting Engineer, Victoria, B.C., Canada specifically for publication in the « Bulletin ».

The quantitative determination of tantalum in ores, concentrates, slags, metals, alloys and carbides is one of the most difficult tasks of the analytical chemist. In nature, tantalum is always accompanied by niobium, and the resemblance in properties of these elements is one of the closest in the entire periodic table, leading to many problems in separation procedures. In tantalum ores, apart from niobium, several or many of the following elements may be found : aluminium, alkalis, antimony, beryllium, bismuth, calcium, iron, magnesium, manganese, phosphorus, samarium, silicon, thorium, tin, titanium, tungsten, uranium, yttrium and zirconium. In metals, alloys and carbides, besides the almost invariable presence of niobium, one or more of the following elements may be present with tantalum : cobalt, copper, iron, magnesium, manganese, molybdenum, nickel, silicon, tin, titanium, tungsten, vanadium and zirconium.

SAMPLING

The refractory nature of tantalum, the low but frequently variable concentration of this element in many of its ores and in metals, alloys and carbides where it is a minor but important constituent, and its high value, necessitate the careful preparation of a finely ground, thoroughly mixed sample. Minerals and ores, concentrates, tin slags and similar materials should be ground to pass a 200-mesh sieve. For metals, alloys and carbides, which are impossible or uneconomic to pulverize to this degree, sample heterogeneity can be minimized by decomposing a large sample, making the solution to a convenient volume, and withdrawing a suitable aliquot for the analysis.

DECOMPOSITION

Tantalum is very resistant to attack by any single acid or even by aqua regia. It is only brought into solution by digestion with hydrofluoric acid, or by fusion with alkali bisulphate, potassium hydroxide or potassium carbonate. Extraction of the solidified melt with tartaric or oxalic acid results in a clear solution containing the tantalum.

SEPARATION

The few methods for the determination of tantalum require the isolation of the latter from nearly every element; separation procedures are very important in the analysis for tantalum.

Many elements can be removed from tantalum by the passage of hydrogen sulphide into a dilute hydrochloric or sulphuric acid solution to precipitate them as sulphides. These include antimony, arsenic, bismuth, cadmium, copper, germanium, gold, iridium, lead, mercury, molybdenum, osmium, palladium, platinum, rhenium, rhodium, ruthenium, silver and tin.

A large number of elements can be separated by cupferronchloroform extraction of tantalum from a cold 10 % hydrochloric or sulphuric acid solution, leaving in the acid layer aluminium, arsenic, barium, beryllium, boron, calcium, chromium, cobalt, germanium, gold, indium, iridium, lead, magnesium, manganese, mercury, nickel, osmium, phosphorus, platinum, rhenium, rhodium, ruthenium, selenium, silver, strontium, tellurium, thorium and zinc. In the presence of a fluoride, cupferron will precipitate tantalum but not tungsten.

Many elements are deposited on a mercury cathode in a dilute solution of sulphuric acid, thereby separating them from tantalum. These include bismuth, cadmium, chromium, cobalt, copper, gallium, germanium, gold, indium, iridium, iron, molybdenum, nickel, palladium, platinum, rhodium, silver, thallium, tin and zinc.

Tantalum does not react with dithizone, and a few elements, if they occur in small amounts, can often be conveniently removed as dithizonates. These comprise bismuth, cadmium, cobalt, copper, gold, indium, lead, mercury, nickel, palladium, platinum, silver, thallium, tin and zinc.

A small group of elements can be removed from tantalum by volatilization : antimony, arsenic, boron, germanium, mercury, osmium, rhenium, ruthenium, selenium and tin.

Tantalum is precipitated by zinc oxide, and a re-precipitation will leave in solution all the cadmium, calcium, germanium, lead, magnesium, manganese, mercury, nickel and silver.

Minor, but often useful, separations include : ether extraction in 1 : 1 hydrochloric acid which separates tantalum from gallium, gold, iron, molybdenum and thallium; sulphur dioxide in hydrochloric acid to precipitate gold, selenium and tellurium; electro-deposition of copper and silver in nitric-sulphuric acid, and of cobalt and nickel in ammonia-ammonium sulphate solution.

In the majority of laboratories throughout the world, the most popular and effective method of separating tantalum is by the technique of ion exchange. There are a number of variations in resins and eluting liquids, depending on the type, number and quantity of elements accompanying tantalum in the sample, but one example will suffice to illustrate the procedure. When a sample solution containing 5 parts hydrochloric acid, 4 hydrofluoric acid, 11 water is passed through a column of Dowex or similar resin, niobium and tantalum are retained whereas virtually all other elements pass through the column. Niobium can be eluted with 14 % ammonium chloride : 4 % hydrofluoric acid solution. Tantalum is finally eluted with 14 % ammonium chloride : 4 % hydrofluoric acid solution, which has been adjusted to pH 5.5 with ammonium hydroxide.

DETERMINATION

Unfortunately, tantalum is much more restricted than most elements in the variety of chemical procedures which can be employed in its determination. Optical spectrography is of little use, for the spectral sensitivity of tantalum is poor. X-ray fluorescence is, similarly, not suitable for this element. Tantalum is insensitive to determination by atomic absorption spectroscopy; it is also subject to complex interference effects in this technique.

Although niobium can be determined volumetrically by passing the sample through a Jones reductor and titrating with potassium permanganate solution, tantalum is not reduced by zinc in acid solution and is not titrated by potassium permanganate.

Finally, any colorimetric procedure proposed to date requires the virtual isolation of tantalum, thereby nullifying the usual advantages of photometric techniques.

The analyst has little choice, then, to employ other than time-honoured but lengthy gravimetric methods, isolating the tantalum and finally weighing it as the pentoxide. As an example, when tantalum has been separated from other elements by ion exchange as outlined in the preceding section, it can be determined by cooling the eluate to below 10 °C, adjusting the hydrochloric acid concentration to about 10 %, adding 15 grams of boric acid and 60 ml. of cold 6 % cupferron solution. Filtration of the tantalum cupferrate, followed by carreful ignition in a platinum crucible at 1100 °C to Ta_2O_5, gives the tantalum content.

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