

Analytical quality control in the production of nuclear grade zirconium and its alloys

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THE chief application of zirconium metal and zircalloys is in nuclear reactor engineering as cladding material for the fuel elements and as structural material in the construction of reactor cores. The selection is based on considerations¹ of low neutron absorption cross section, fabricability, corrosion resistance and mechanical strength at elevated temperatures. These properties are, however, sensitive to impurity levels and alloying compositions. For example, for neutron economy the hafnium and boron contents should be within 200 ppm and 0.5 ppm respectively; for corrosion resistance the aluminium, carbon and nitrogen tolerances are respectively only 75 ppm, 500 ppm and 50 ppm; and for ease of fabrication the maximum permissible oxygen content is 1500 ppm. In the large scale production of zirconium sponge and zircaloy ingots, it becomes therefore essential to have a strict control of impurity levels in the successive stages of the batchwise production, in order to ensure consistency of quality and performance in the finished product.

Specification

Of the two known minerals of zirconium viz. zircon and baddeleyite, only zircon is available in large quantities in India. The composition of zircon is shown in Table I.

The specifications for reactor grade zirconium sponge² and zircalloys³ are given in Tables II and III respectively.

Process description

Production of zirconium oxide

The production of nuclear grade zirconium oxide from zircon involves caustic fusion and leaching to remove silica, dissolution in nitric acid and solvent extraction of zirconium with tributyl phosphate, for the removal of hafnium and other impurities. The extract is scrubbed with nitric acid to remove the small amounts of hafnium

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SYNOPSIS

The paper discusses the importance of analytical quality control in the various stages of tonnage-conversion of Indian zircon successively into pure zirconium oxide, zirconium sponge metal, zircaloy ingots and tube products, to meet stringent nuclear specifications. A general scheme of sampling is presented for the different stages. Methods of analysis of various impurities in zirconium intermediates and zirconium metal and alloying elements in zircaloy are discussed.

and other impurities present. Pure zirconium nitrate is finally transferred to the aqueous phase using dilute sulphuric acid, precipitated as hydroxide and calcined at 800°C. The raffinate containing the hafnium and other impurities is processed to obtain pure hafnium.

Production of zirconium sponge

For conversion to metal, the zirconium oxide is chlori-

TABLE I Composition of Indian zircon

Constituents	%
*ZrO ₂ +HfO ₂	65.5 to 66.5
SiO ₂	31.0 to 32.0
Al ₂ O ₃	0.70
Fe ₂ O ₃	0.1 to 1.0
TiO ₂	0.3 to 1.5
ThO ₂	0.02
P ₂ O ₅	0.1

*Hafnium content is about 2.5 per cent expressed as

$$\frac{\text{HfO}_2}{\text{ZrO}_2 + \text{HfO}_2} \times 100.$$

TABLE II Specifications for reactor grade zirconium sponge

Element	Impurity limit ppm	Element	Impurity limit ppm
Al	75.0	Mo	50.0
B	0.5	N	50.0
C	500.0	Na	50.0
Ca	30.0	Ni	70.0 (40 ppm for Zr-4 base material)
Cd	0.5	O	1400.0
Cl	1300.0	P	100.0
Co	20.0	Pb	100.0
Cr	200.0	Rare earths	15.0
Cu	50.0	Si	100.0
Fe	1500.0	Ti	50.0
Hf	100.0	U	3.5
Li	1.0	V	50.0
Mg	600.0	W	50.0
Mn	50.0	Sn	100.0

Size of sponge ... -3/8 inch, +20 mesh
 Hardness of arc-melted buttons ... 150 BHN (3000 kg load)

nated in the presence of carbon and after reduction of the zirconium tetrachloride with magnesium by the Kroll process, the magnesium chloride and excess magnesium are removed by vacuum distillation. As this process involves batch operations, there is some variation in sponge quality from batch to batch and even in each batch there is a gradation in impurity content⁴ depending on the location of the sponge in the reduction pots.

Generally, the metal that is formed in the early stages of the reduction is deposited as a thick plate near the bottom analysing high in iron, nitrogen, etc. The bulk of the sponge corresponding to reactor grade specifications is obtained in the form of dense massive chunks. The material that is formed towards the fag end of the reduction is light and porous and holding relatively large amounts of magnesium. In addition, in individual runs there may be material that does not conform to any of the above categories. Prior to melting, it is necessary that the different grades of sponge are individually sampled and analysed and based on the analysis, blends prepared to correspond to the reactor grade specifications.

TABLE III Zircaloy ingot specifications

Element	Composition	
	Zircaloy-2	Zircaloy-4
Zirconium (minimum) based on difference	97.7%	97.7%
Alloying elements		
Sn	1.2-1.7%	1.2-1.7%
Cr	0.05-0.15%	0.05-0.15%
Fe	0.07-0.20%	0.12-0.18%
Ni	0.03-0.08%	0.004% (max.)
Fe+Cr+Ni	0.18-0.38%	—
O	0.10-0.14%	0.10-0.14%
Impurity elements		
Al	75 ppm	75 ppm
B	0.5 "	0.5 "
C	500 "	500 "
Cd	0.5 "	0.5 "
Co	20 "	20 "
Cu	50 "	50 "
H	25 "	25 "
Hf	100 "	100 "
Pb	130 "	130 "
Mg	20 "	20 "
Mn	50 "	50 "
Mo	50 "	50 "
N	70 "	70 "
Si	120 "	120 "
Ti	50 "	50 "
U	3.5 "	3.5 "
V	50 "	50 "
W	100 "	100 "
Hardness	187 BHN (3000 kg load)	187 BHN (3000 kg load)

Zircaloy fabrication

The zirconium sponge with the alloying elements is

briquetted and used as consumable electrodes for making zircaloy ingots by double arc melting in vacuum. The end portions of the ingots are cut off and the rest is machined to the required size and fabricated into tubes, plates, wires, and other sections as required. The conversion efficiency of zirconium sponge into finished zircaloy components is about 40 per cent. About 60 per cent of the scrap if carefully handled can be available for re-fabrication. The rest of the scrap—still low in hafnium, but contaminated with other impurities like oxygen, carbon, and nitrogen—can be chemically re-processed back to ductile zirconium sponge.

Scheme of sampling

An efficient sampling programme, especially for zirconium sponge⁵ in which there is considerable segregation of impurities, is essential to give a proper meaning to the analytical results.

The proposed sampling and analytical scheme in the tonnage production of zircaloy tubes, according to a process flow-sheet described in Section 3, is given in Table IV.

The procedures intended to be followed for chemical and spectrochemical analysis of the various zirconium intermediates and metal products, in the tonnage production of zircaloy tubing starting with zircon sand, are described in the sequel.

Chemical methods of analysis

Analysis of zircon

The zircon concentrate for the production of ZrO_2 is available from the beach sand beneficiation plants at Kerala. As a certain amount of contamination with titanium, thorium and silicon minerals may be expected in the concentrate, the impurity contents and a minimum $ZrO_2 + HfO_2$ content has to be specified.

Silicon, aluminium, phosphorus and zirconium-hafnium

For purposes of estimating silicon, aluminium, phosphorus and (Zr+Hf) in zircon sand the sample is first fused with Na_2O_2 . The silicon is separated by fuming with sulphuric acid and further leaching with HCl and estimated as SiO_2 . The leach solution is treated with NaOH and the precipitated hydroxides are separated by filtration. The filtrate is used for the estimation of aluminium as the oxinate and phosphorus by the phosphomolybdate method. The precipitate, after acid dissolution and reprecipitation with ammonia, is brought into solution with HCl and (Zr+Hf) is precipitated as the mandalate⁶, ignited and estimated as the oxide.

Titanium and iron

For estimating titanium and iron in zircon sand the sample is fused with sodium fluoride and boric acid and extracted with sulphuric acid. After driving off the

fluoride and dissolving the residue in water, one portion of the solution is used for estimation of iron⁷ by reduction with hydroxylamine hydrochloride and colorimetric estimation using O-phenanthroline reagent, and another part of the solution is treated with phosphoric acid to complex the iron, and titanium⁸ is estimated colorimetrically using hydrogen peroxide.

Thorium

Thorium contamination in zircon originates from monazite. To determine the thorium content the sample is fused with Na_2O_2 and the hydroxides are precipitated with ammonia. After acid dissolution, reprecipitating the thorium as the iodate, it is ignited and dissolved in HCl and estimated colorimetrically using Thoron reagent. Interferences from iron and zirconium are avoided by the addition of hydroxylamine hydrochloride and tartaric acid to the solution.

Analysis of zirconium oxide

In the chemical purification plant the zirconium solution has to be tested for all impurities including hafnium, at the various stages of purification. As the impurity levels are low, spectrographic methods as described in section 7 are mostly employed. However, occasional check analyses are done chemically for estimating the Si, Fe and U contents. The rare earths in pure zirconium solution are estimated spectrographically, after chemical separation and preconcentration.

Iron

The iron in pure zirconium solution is determined by the same method as described under titanium and iron.

Silicon⁹

Silicon present in trace amounts in zirconium is determined by first dissolving the sample and converting the silicon to a reactive form using hydrofluoric acid. The silicon is reacted with molybdic acid to form molybdisilicic acid, which is then reduced to a heteropoly blue complex using a reducing solution consisting of $NaHSO_3$, NaOH and 1-amino-2-naphthol-4-sulphuric acid. Spectro-photometric measurements are made at 8150 Å.

Uranium^{10,11}

The uranium, from a nitrate solution of the sample, is extracted with ethyl acetate using aluminium nitrate as the sorting reagent. An aliquot of the extract is fused with a mixture of sodium carbonate (80 parts) and sodium fluoride (20 parts) and the fluorescence exhibited by the uranium is measured with a photo-electric fluorometer.

Rare earths¹²

The rare earths and yttrium carrier, which also serves

TABLE IV Sampling and analytical scheme

Source of sample	Analysis required	Type of sampling proposed
<i>A. Zircon concentrate</i>		
	ZrO ₂ and HfO ₂ content and amount of impurities like Si, Al, Fe, Ti and U	Each batch of zircon is to be checked to meet specifications.
<i>B. Zirconium oxide plant</i>		
(a) Cake obtained after fusion	Zr+Hf content and moisture	—
(b) Nitrate solution	Zr+Hf concentration, free acidity and Si content	—
(c) Extract before and after scrubbing stages	Zr, Hf and Si contents and free acidity	—
(d) Raffinates from extraction and scrubbing stages	Zr, Hf and Si contents and free acidity	—
(e) Pure zirconium solution, zirconium hydroxide and zirconium oxide	Estimation of Hf, U, rare earths and other metallic impurities	—
(f) Hafnium oxide	Estimation of Zr and other metallic impurities	—
<i>C. Zirconium sponge plant</i>		
(a) Sponge lot	Estimation of carbon, Cl, Mg and other common metallic impurities	The daily sponge output is graded according to the types of sponge and divided into 50 kg lots. 1 kg samples are taken from each lot and briquetted. Drillings are taken from four points in each briquette and evaluated.
(b) Buttons	Estimation of O, H, N and hardness testing	Two samples are taken from each lot and are melted in argon atmosphere.
(c) Evaluation ingot	Estimation of C, O, H, N and other common metallic impurities and hardness testing	The sponge lots are blended in 500 kg batches according to the analysis report and for each blend an evaluation ingot is consumably melted by taking a 20 kg sample.
<i>D. Zircaloy fabrication plant</i>		
(a) Final skimming operation of the remelted ingot	Testing the homogeneity of alloying composition and estimation of C, O, H, N and metallic impurities	Drillings from the final skimming operation of the re-melted ingot are taken from different points and briquetted and faced to give ½" dia. pellet samples.
(b) Edge slices	Testing the homogeneity of alloying composition and estimation of C, O, H, N and metallic impurities	Four slices are cut from the edges of each finished ingot and each slice is sampled at three points after facing.
(c) Finished tubes and plates	Testing the homogeneity of alloying composition, estimation of C, O, H, N and metallic impurities, metallographic examination and mechanical and corrosion tests	One sample is taken from every lot of 100 of finished components.
(d) Scrap	Alloying composition and estimation of C, O, H, N and other impurities	The scrap is chopped to size, classified in 50 kg lots and two evaluation buttons are melted from each lot.

as internal standard for spectrographic analysis, are separated from zirconium by passing the hydrofluoric acid solution of the metal through a cation exchange column. The rare earths and the carrier are then purified by a double fluoride precipitation and converted to the oxide for further analysis by the spectrographic method (Section 7. 2.3).

Analysis of zirconium sponge

The major impurities in zirconium sponge are the unreacted magnesium metal and chlorine in the form of chlorides. These are determined chemically, whereas the purity of the sponge with regard to other metallic impurities are tested spectrographically. In addition, it is necessary to check the gaseous impurities and the carbon content of sample buttons got by arc melting representative samples of the sponge in an argon atmosphere.

Magnesium¹³

Magnesium is determined flame photometrically after separating zirconium by ion-exchange and iron by electrolysis.

Chlorine¹⁴

The chlorine in zirconium sponge is determined potentiometrically by dissolving the sample in hydrofluoric and nitric acids and by using silver nitrate as the titrant.

Nitrogen¹⁵

Nitrogen in zirconium metal and zircalloys is determined by the 'Kjeldahl method'. After dissolving the sample in hydrofluoric acid the solution is made highly basic with sodium hydroxide and the nitrogen is separated as ammonia by steam distillation. Ammonia in the condensed solution is determined colorimetrically using Nessler's reagent.

Determination of alloying elements in zircalloys

The zircaloy ingots and the finished components are to be checked for homogeneity of distribution of the alloying elements (Sn, Fe, Cr and Ni), in addition to the amounts of impurity elements. This is mainly done using the Direct Reading Spectrometer but, occasional chemical checks are carried out on the spectrometric results. For the estimation of gaseous impurities and carbon, the methods followed in the case of zirconium sponge are adopted.

Tin¹⁶

The sample is dissolved in hydrofluoric acid and the fluoride ion is complexed with boric acid. Tin is reduced with metallic antimony or aluminium in an atmosphere of carbon dioxide and the stannous tin is determined by titration with standard iodate-iodide solution using the starch iodine system as the indicator.

Iron

Iron is determined by the orthophenanthroline method as described in Section 5.1.2.

Chromium¹⁷

Samples are dissolved in hydrofluoric and sulphuric acids and the fluorides are removed by fuming. Chromium is determined by oxidation to dichromate with persulphate and by measuring the intensity of the complex formed with diphenyl carbazide.

Nickel¹⁸

The sample is dissolved in hydrofluoric and sulphuric acids and the fluoride ion is eliminated by repeated evaporation to SO₃ fumes. The nickel in the final solution is oxidised to the trivalent state using bromine and citric acid and then complexed with dimethylglyoxime. The optical density is measured at 5400 Å.

Estimation of carbon, oxygen, hydrogen and nitrogen

Carbon

The carbon in zirconium is estimated by burning the sample in an oxygen atmosphere and measuring the carbon-dioxide so formed either by the conductometric method¹⁹ using Ba(OH)₂ solution or by the thermal conductivity method using He as the carrier gas or by the low-pressure method²⁰ using a slush bath of isopentane cooled in liquid air to separate CO₂ from the oxygen stream.

Oxygen, hydrogen and nitrogen

The vacuum fusion method is generally used for evolving the gases—oxygen as CO and hydrogen and nitrogen as molecular gases. The total pressure is measured and by estimating CO by infrared absorption method and hydrogen by thermal conductivity method nitrogen is got by difference. Because of the difficulties involved due to the incomplete extraction of nitrogen from zirconium, the Kjeldahl method as described in Section 5.3.3. is used for more accurate determination of nitrogen wherever necessary.

Spectrographic analysis

Determination of hafnium-zirconium ratios

Zirconium and hafnium oxides, being highly refractory, do not burn uniformly in an arc and it is even more difficult to excite the hafnium lines. Also, there is always a continuum, accompanying the Zr/Hf spectra, which reduces the line to background ratio of the hafnium lines at low hafnium concentrations. A buffer consisting of barium fluoride and graphite has been found²¹ to be useful in getting a reproducible burning of the arc and in reducing the background. However,

one of the most intense hafnium lines, namely Hf 2641, which lies in a lower background region as compared to the other intense line Hf 2820, is interfered²² by a barium line. This can be avoided by using strontium fluoride instead of barium fluoride for the low hafnium samples. Hafnium and zirconium lines can be used as internal standards for each other because of their similarity in behaviour in the arc column.

Low hafnium in zirconium

For hafnium contents in the range of 50–1000 ppm, the zirconium sample in the oxide form is mixed with strontium fluoride and graphite in the ratio 2 : 0.5 : 0.5 and 15 mg of this mixture is burned in a D. C. arc at 25 amps current using a neck-type shallow cup electrode and an argon atmosphere. A grating spectrograph, giving a dispersion of $<2.5 \text{ \AA/mm}$ in the first order and blazed at 3000 \AA , is used for photographing the spectra, the exposure being 60 sec. with a prearc of 15 sec. Both the line pairs Hf 2641/Zr 2681 and Hf 2820/Zr 2681 are used for this concentration range.

Hafnium-zirconium ratios

The estimation of Hf/Zr, in the range of 0.1 to 99.9%, is carried out by using barium fluoride and graphite as the buffer and exciting the spectra at 16 amps D. C. in an air atmosphere. Different low intensity lines could be used to cover entire concentration range and a spectrograph of lower dispersion could be used for photographing the spectra.

Determination of metallic impurities and alloying elements in zirconium oxide and hafnium oxide

The carrier distillation method usually employed for the estimation of impurities in refractory oxides is not very satisfactory in the case of zirconium and hafnium oxides because the Zr/Hf spectra are not completely suppressed by the carrier and some of the impurities do not come into the arc reproducibly. Direct burn methods have been found to be more sensitive and reproducible. Different buffers are used for the estimation of common impurities, rare earths and alloying elements in zirconium oxide and hafnium oxide. In the reclamation process of zircaloy scrap back to usable metal it would be necessary to analyse samples containing high concentrations of alloying elements. This is done by converting the sample into the oxide form.

Common metallic impurities in zirconium oxide

The sample is mixed with barium fluoride in the ratio 4 : 1 by weight and 15 mg of this mixture is excited in a shallow cup electrode using a D.C. arc of 12 amp. The exposure is limited to the steady period of first 15 secs. A Hilger large quartz spectrograph or a 3.4 meter grating spectrograph giving a dispersion of 2.5 \AA/mm in the first order is used for photographing

the spectra covering the region of 2200 \AA – 3300 \AA . Gallium and germanium, added along with the barium fluoride, act as internal standards for the estimation of the following elements covering the concentration ranges usually present in reactor grade zirconium : Al, B, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Ph, Si, Ti, V and W. A different region of the spectrum is used for samples needing Li and Na estimation.

Estimation of common metallic impurities in hafnium oxide

The sample is mixed with strontium fluoride in the ratio 9 : 1 and a 20 mg charge is burned in a shallow cup electrode at 16 amps D.C. The steady period of 13 sec. is used for photographing the spectra on a Hilger larger quartz spectrograph or a 3.4 meter grating spectrograph.

Estimation of rare earths in zirconium and hafnium

The rare earths along with yttrium carrier are first separated and purified as described in section 5.2.4. The oxide so obtained is mixed with graphite and excited in a shallow cup electrode using a D.C. arc of 16 amps. A 3.4 meter grating spectrograph giving a dispersion of $<2.5 \text{ \AA/mm}$ is used to reduce the continuum and line interference in the 3300 – 4300 \AA region that is photographed. Yttrium itself is used as the internal standard.

Analysis of zircaloy scrap for alloying elements by the D.C. arc method²³

The zircaloy sample is converted to the oxide and mixed with zinc oxide and graphite in equal portions by weight. A 10 mg charge is excited in a D.C. arc at 10 amps. using shallow cup electrodes. Cobalt is used as the internal standard for the four alloying elements—Sn, Fe, Cr and Ni.

Analysis of zircaloys using a direct reading spectrometer

The main advantage of a direct reading spectrometer for routine quality control analysis is the speed and accuracy with which the results are obtained. In a metal/alloy production facility, where numerous determinations are to be carried out each day, the wet chemical methods and even the spectrographic methods are replaced by the direct reading techniques, which enable the analyses of as many as 100–200 samples per shift, depending upon the type of excitation and read-out and the number of impurities to be determined in each sample.

Principle

The analysis of a sample on the direct reading spectrometer involves excitation and measurement of the spectrum of the material and calibration with known

TABLE V Analytical lines for zirconium and zircaloy analysis using a direct reading spectrometer

Serial no.	Element	Concentration range in ppm	Wavelength	Possible interference	Remarks
1.	Al	20-2000	3082.16 × 2*	V 3082.11 × 2 & Mn 3082.05 × 2	The aluminium line is very sensitive and interference from the low intensity vanadium and manganese lines are negligible.
2.	B	0.2-2.0	2497.73 × 2	Fe 2497.82 × 2	The intensity of the Fe line is very low even at the 2000 ppm level (in alloys). The only other boron line at 2496.8 is interfered by Zr 2426.48 and Fe 2496.53.
3.	Ca	20-1000	4226.73	Cr 4226.75 & Fe 4226.43	As the calcium line is very sensitive interference from Cr and Fe are negligible.
4.	Cd	0.2-2.0	2288.02	—	—
5.	Cr	20-2000	3021.56	—	—
6.	Co	20-200	3453.50 × 2	Cr 3453.33 × 2, Cr 3453.74 × 2 & Zr 6907.37	The chromium lines are of very low intensity and so do not interfere. Interference from zirconium is avoided by using a filter. The high back-ground in this region is reduced by using the second order. Co 2521.36 can be used alternatively.
7.	Cu	20-500	3247.5	—	—
8.	Hf	50-1000	2641.41 × 2 & 2820.22 × 2	—	—
9.	Fe	20-5000	2599.4	—	—
10.	Pb	20-200	4057.8 × 2	—	The high background in this region is reduced by using 2nd order.
11.	Mg	10-1000	2802.7 × 2	Co 2802.7 × 2	Co will not be usually present in zirconium samples.
12.	Mn	10-200	2801.06	Zn 2801.06 & Zn 2800.87	Zn will not be usually present in zirconium samples. Zn lines are of low sensitivity compared to the very sensitive Mn line.
13.	Mo	20-200	3170.35	—	—
14.	Na	10-500	5890.0	—	—
15.	Nb	20-50000	3195.0	—	—
16.	Ni	20-1000	3050.8 × 2	Hf 3050.76 × 2	Hafnium will be absent in nuclear grade zirconium.
17.	Si	20-1000	2516.1 × 2	—	—
18.	Sn	20-20000	2840.0 × 2	Ba 5680.20 & Ti 5679.94	First order interference from Ba and Ti is eliminated by using filter.
19.	Ti	20-1000	3349.4 × 2	Cr 3349.32 × 2	Cr line is of low intensity and does not interfere with the intense titanium line.
20.	V	20-200	3185.40 × 2	—	—
21.	W	20-200	4008.87	—	—
22.	Zr	Internal standard			

*denotes second order

standards. The main components of the instrument are the excitation source, the spectrometer and the read-out system. The sample is struck with electric discharge, derived from the source unit, and a small amount of the sample is vapourised. The atomic spectrum that is emitted is dispersed by means of the spectrometer, consisting of a grating or a prism as the dispersing element, and the particular wavelengths of the elements of interest are isolated using exit slits suitably positioned on the focal curve. The light passing through each slit is directed on to a photomultiplier tube to produce a current proportional to the intensity of the emitted radiation which in turn is a function of the concentration of the particular element in the sample. Outputs from the photomultipliers are integrated by capacitors during exposure and when the exposure ends the potentials of the capacitors are measured one after the other using the read-out system.

Calibration

The spectrometer is calibrated by running standards of known composition and obtaining a calibration on graph by plotting the voltages obtained as a function of concentration. Samples of varying impurity contents, which are repeatedly analysed by chemical and spectrographic methods to provide reliable values for the compositions, are used as primary standards for the above calibration. The primary calibration is maintained from day to day by running reference samples whose analyses have been done relative to the primary standards.

Accuracy of results

The accuracy of the spectrometric results depends upon (i) the accuracy of analysis of the primary standards, (ii) the homogeneity of the primary standards as well as samples, (iii) the reproducibility of sample preparation, (iv) stability of the spectrometer and measuring unit and (v) stability of the excitation source. These factors can be controlled by taking proper care in preparation of primary standards, and samples, by choosing and maintaining proper excitation conditions and by controlling the temperature and humidity of the laboratory.

Choice of spectrometer

The choice of the spectrometer is generally governed by the matrix element and the impurities/alloying elements that are to be estimated. For the determination of trace elements the number of analytical lines available are very limited and, in a matrix like zirconium having a large number of lines, interferences are to be avoided. The chosen lines should be at a minimum distance apart from one another so as to accommodate the exit slits. With a grating spectrometer it is possible to use some of the lines in the second order provided the grating is blazed to a suitable region. The selection of lines for the alloying elements is not a problem because of the higher concentration levels involved. For zirconium analysis, a grating spectrometer covering a region of

2000 Å to 8500 Å and having a dispersion of about 5 Å/mm in the first order is satisfactory.²⁴ The suitable analytical lines are given in Table V along with the possible interfering lines. Whereas in most cases the 'Ray Ultimate' lines are chosen, for the others it is possible to choose alternate lines according to the convenience in mounting the exit slits and photomultiplier tubes. Suitable zirconium lines are chosen as internal standards when the ignited A. C. arc is used to excite the spectra by the point to plane technique.

Conclusion

It will be apparent from the above discussion that the production of zircaloy components for nuclear applications has to be supported by a large-scale analytical control programme, keeping a strict watch on quality from batch to batch. As the ultimate performance of the various zircaloy components will be dictated by the purity and homogeneity of the alloy ingots and as many of the zircaloy components in the core of the reactor have to last for the lifetime of the reactor, such a close quality control is fully justified to ensure reliability in service. A rough estimate on the cost figures shows that analytical quality control alone would contribute about 4% to the cost of the finished zircaloy products.

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