A New ICP-OES Method for estimating Impurities in High Purity Nb_2O_5 and Nb Metal without matrix separation

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Abstract

This paper deals with the development of a method for determination of 45 impurity elements in high pure niobium oxide (Nb_2O_5) and high pure niobium (Nb) metal using ICP-OES without separation of matrix (Nb). High pure niobium (Nb) metal is used in the production of Zr-2.5% Nb alloy for manufacturing PHWR core structural pressure tubes. Also, high pure Niobium (RRR grade) is used in manufacturing of super conducting radio frequency cavities, which are crucial components in particle accelerators. The effect of Nb matrix on elemental sensitivities and S/B was evaluated at different matrix concentration is discussed. The method has been validated using standard recovery, calculated by spiking a niobium sample and measuring the resultant concentration. It was observed that a recovery of 95-105% obtained for all the elements. Typical samples of high pure Nb_2O_5, pure Nb metals are analyzed and the results have shown a % RSD found to be less than 3% for all the elements of interest.

Key words: Niobium pentoxide, Niobium metal, ICP-OES, RRR, PHWR

1. Introduction

Being a refractory metal with exceptional properties like high melting point, corrosion resistance and superconductivity, Niobium (Nb), finds a place in several high-tech applications. They include making of superconducting magnets, high-strength low-alloy steels and aerospace components. Nuclear Fuel Complex (NFC) produces high pure niobium metal through a series of chemical conversion processes using columbite-tantalite (CT) ore as raw material. The chemical conversion process involves acidic dissolution of CT ore followed by solvent extraction to separate niobium from tantalum. Extract rich in tantalum and raffinate rich in niobium are generated during solvent extraction process. The

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niobium rich raffinate is taken for further chemical processes like precipitation, acid dissolution, solvent extraction, stripping, precipitation and pyro-hydrolysis to get niobium pentoxide (Nb_2O_5). Since there is a possibility of introducing several impurities during the chemical conversion process, the quality requirements for Nb_2O_5 are maintained at the same level as those for high purity Nb metal, as shown in Table 1. Therefore, a homogeneous Nb_2O_5 sample is taken for the analysis at this stage. Subsequently, Nb_2O_5 is reduced to Nb metal using alumino-thermit reduction process. Since Nb metal is very hard to crush, hydriding and de-hydriding process is resorted to make Nb granules, which are subjected to vacuum distillation to get high pure Niobium metal. The production process flow sheet is shown in **Fig.1**.

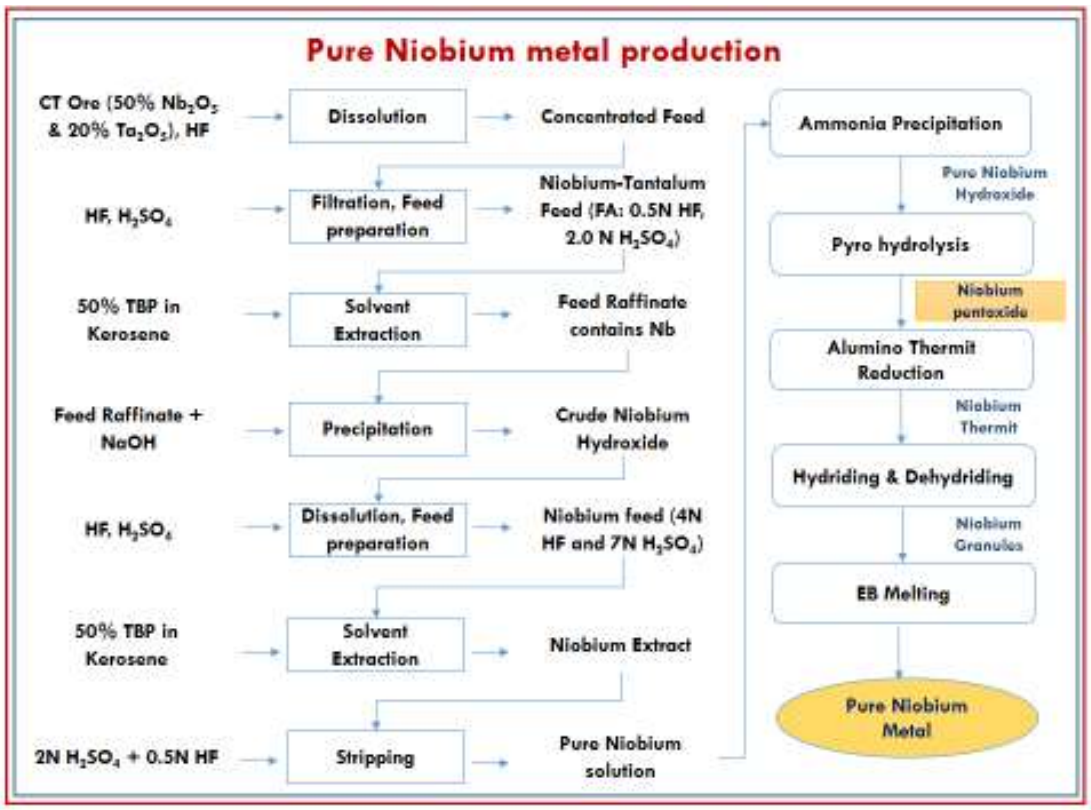

Fig. 1. Process flow sheet for Nb_2O_5 and Niobium metal production

The pure niobium metal is used as alloying element in Zr-2.5% Nb alloy to fabricate pressure tubes (PTs) at NFC for all operating Indian Pressurized Heavy Water Reactors (PHWRs) and Boiling Water Reactors (BWRs) through well-established process of melting and tube preparation process. Requisite quantity of niobium metal is added to zirconium metal during melting for producing the Zr-2.5%Nb alloy. Further to this, high pure niobium

metal is also used in the fabrication of superconducting devices. Niobium (Nb) being an important metal used in production of PT and superconducting devices, its purity will have influence on desirable properties of these products. For example, Residual Resistivity Ratio (RRR) value gets affected by chemical purity of Nb metal [1,2] used for superconducting devices. Similarly, the beneficial properties of PTs like corrosion resistance, creep strength are severely impaired by purity of Nb metal used in their production. In view of this, stringent specifications have been laid down for all the in-put materials including niobium metal, detailed in Table 1. Therefore, it is mandatory to monitor the chemical quality of niobium metal with respect to Al, B, Be, Cd, Co, Cr, Cu, Fe, Hf, Mg, Mn, Mo, Ni, P, Pb, Si, Sn, Ta, Ti, V, W, Zr as integral part of Quality assurance/Quality Control (QA/QC) program.

Table 1 Specification limits for Niobium metal

Element	Specification limits for PT (ppm)	Specification limits for superconductors (ppm)	Element	Specification limits for PT (ppm)	Specification limits for superconductors (ppm)
Fe	500	30	Al	100	30
Mo	100	50	V	100	30
Ni	50	30	Cr	100	30
Si	100	30	Mn	200	30
Ta	1000	500	Co	20	30
Ti	100	40	Cu	50	30
W	500	70	Zr	-	30
Mg	100	30	Cd	20	30
B	5	-	P	100	-
Be	50	-	Hf	200	-
Pb	200	-	Sn	100	-

Several methods such as direct injection ICP-MS, electro thermal vaporization ICP-MS, ICP-OES, neutron activation analysis (NAA), Graphite Furnace Atomic Absorption Spectrometry (GF-AAS), X-ray Fluorescence (XRF) are cited in literature for determination of various trace impurities in high pure niobium metal. A method of fluorination assisted

electro thermal vaporization inductively coupled plasma mass spectrometry (FETV-ICP-MS) to determine Ta, Ti, Cr, W, Ni, Cu and Mn directly in niobium pentoxide powder was cited [3]. A neutron activation combined with group separation based on anion-cation exchange procedure was cited for determination of 33 trace impurities in niobium metal was cited in [4]. A method has been described for on-line matrix separation and direct injection/inductively coupled plasma mass spectrometry procedure involving determination of 52 elements in niobium metal [5]. However, quantitative separation was achieved for only 25 elements, while the remaining 27 elements were determined in presence of matrix after appropriate dilution. A laser ablation ICP-MS procedure for determination of Mg, Al, Si, Ca, Ti, Mn, Fe, Ag, Sn, Ta, W in niobium oxide samples was cited in [6]. Also, a sorption pre-concentration based GF-AAS method has been reported in literature for determination of impurities in Nb_2O_5 [7]. Mezhevaya et.al. have reported an XRF based method for determination of Fe, Ta, Nb and Cu in Niobium based materials[8]. However, this method suffers from memory effects and poor reproducibility. A method for direct determination of 28 trace impurities in niobium metal using ICP-OES without any prior separation of matrix has been cited in [9]. However, determination of rare earth elements (REEs) which have very high neutron absorption values and very much detrimental effects on the application of PTs in nuclear reactors was not discussed. The above cited methods have either followed a prior matrix separation procedure or modification of procedure before the analysis of impurities in niobium metal and niobium oxide. Further, NAA method requires nuclear reactor facility in the premises of testing lab, which is a severe limitation by itself. The LA ICP-MS requires highly skilled operators and also suffers from poor reproducibility. The methods involving matrix separation are tedious and time consuming and not suitable choice for an industrial analytical laboratory attached to production plants operating on round the clock basis to clear the high sample load to meet the production demands.

In view of this, an attempt has been made successfully to develop a simultaneous ICP-OES method to determine trace impurities like Al, B, Be, Cd, Co, Cr, Cu, Fe, Hf, Mg, Mn, Mo, Ni, P, Pb, Si, Sn, Ta, Ti, V, W, Zr, REEs in niobium metal without the prior separation of matrix. Determination of REEs in Nb metal is very important for its application in nuclear industry. High temperature plasma source, simultaneous detection & quantification of multiple impurities with adequate precision & accuracy are the major advantages of ICP-OES. However, the major problem in ICP-OES analysis of niobium metal is spectral interferences from niobium matrix, as it gives complex line rich emission spectra. In view of

this, several wavelengths for each impurity element were profiled and S/B ratio was calculated at different conditions for arriving at the sensitive and interference free wavelengths which could meet the required detection criteria without the separation of matrix. Also, effect of niobium matrix at different concentrations on the detection of impurities mentioned above were also studied and discussed for providing complete insight about how matrix concentration could affect emission intensities of various impurities. Optimization of different instrumental operating conditions like, RF power applied to ICP plasma, plasma gas flow rate, nebulizer gas flow rate, sheath gas flow rate, height of torch, matrix concentration were carried out to achieve required sensitivity levels for various impurities. The method developed is precise and provides enough sensitivity in presence of matrix for all the elements under study. Our method is rapid and does not require any separation of matrix, hence it enables high sample throughput which is the main requirement for an industrial laboratory where sample load is high and timely reporting of results is mandatory to meet the production schedules. Also, REEs have also been determined successfully with adequate precision and sensitivity for the developed method. Total of 45 elements could be successfully determined in presence of matrix by optimizing several parameters as mentioned above.

2. Experimental

2.1 Instrumentation

ICP-OES: Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), (Model: Ultima 2 CHR Make: Horiba Jobin Yvon) with holographic grating of 4320 grooves/mm was employed in the analysis. High salt nebulizer, teflon spray chamber, polypropylene sheath gas system, alumina injector tube, peristaltic pump etc., are part of ICP-OES. After optimization of instrumental conditions RF generator power of 1000 W; plasma gas flow of 12 L/min; nebulizer flow of 0.9 L/min and viewing zone of 15 mm above the load coil was fixed for the analysis.

Micro-wave digestor: Microwave digestion system (Model: ETHOS-1600) was used for digestion of samples. It is s equipped with dual Magnetron system for homogenous microwave power distribution in the cavity. Microwave Power is 1600 watt (two magnetrons minimum 800W each) with Rotating diffuser for evenly distribution of micro*w*ave ensures complete digestion of the samples. Large microwave cavity of 45 Lt.s to accommodate gasses escaping providing safety was provided with system. The system was provided with High pressure, high temperature vessels which can withstand (300^{o}C and 100

bar pressure) especially suitable for digestion of refractory samples. Each vessel is equipped with vent and reseal technology which works in case of excess pressure. Ethos-1600 is made up of stainless steel body and cavity is coated with 5 layers of PTFE which prevents corrosion.

2.2 Preparation of samples

Niobium Metal:

Niobium chippings samples as received from plant were cleaned with acetone/alcohol. Approximately 1gm sample was weighed in a polythene beaker and dissolved in 5ml of HF and 5ml of HNO_3. Subsequently, the solution was made up to 100 ml using ultra high quality (UHQ) water (resistivity 18.2 megaohm.cm). An aliquot of 25ml from this was taken and finally made up to 50 ml with 1N HNO_3. 1% HF was maintained to prevent hydrolysis of Nb.

Niobium pentoxide:

0.25 gm sample was taken in microwave digestion vessel and 1ml HF + 1ml HNO_3 was added. It was subjected to microwave digestion with applied power of 388 Watt, pressure 0.2 bar for 7 minutes and was left for cooling. The vessel was opened after cooling and the volume was made to 50 ml using UHQ water. From this, 10 ml of aliquot was taken in 25 ml volumetric flask and the solution was made up to the mark with 1N HNO_3 for ICP-OES analysis. 1% HF was maintained to prevent hydrolysis of Nb.

2.3 Preparation of standards

Standard addition method was followed for the preparation of matrix matching standards. Pure elemental standards (M/s SCP Science) were used for the preparation of the following standards as shown in Table2. Niobium matrix concentration was maintained at 5mg/ml in all the standards and concentration of individual elements was maintained in all standards as shown in the Table 2. 1% HF and 1N HNO_3 was maintained in all the standards.

Table 2 Composition of standards in 5 mg/mL Nb Matrix

Elements	**Calibration blank**	**Standard2**	**Standard3**	**Standard4**
Fe, Ta, Zr (µg/ml)	0	1.0	2.0	5.0
Al, Hf, Mn, Co, Cr, Cu, Mg, Mo, Ni, Sn, Ti, V (µg/ml)	0	0.2	0.5	1.0
W, Si, Pb, P (µg/ml)	0	0.2	0.5	1.0

Ce, Dy, Er, Eu, Gd, Ho, La, Nd, Sc, Sm, Tb, Tm, Y, Lu, Pr (µg/ml)	0	0.5	1.0	2.0
Ba, K, Na, Sb, Sr, Zn, Bi (µg/ml)	0	0.2	0.5	1.0

2.4 Selection of wavelengths for analytes

Wavelength selection plays significant role in the method development. Any interference from matrix or other elements hamper the analysis and sensitivity levels. As niobium is having line rich emission spectra, several wavelengths of impurities were profiled for choosing the sensitive and interference free wavelengths. Interference free wavelengths for all the 45 elements of interest were tabulated along with their background correction positions as shown in Table 3.

Table 3 Wavelengths chosen for analytes in Niobium matrix

Element	Wavelength (nm)	Element	Wavelength (nm)	Element	Wavelength (nm)
Fe	238.204	Zr	339.198	Ce	413.380
Mo	280.280	Cd	226.502	Dy	353.170
Ni	231.604	Hf	282.022	Er	349.910
Si	251.611	Pb	405.783	Eu	381.965
Ta	240.063	B	208.959	Gd	342.247
Ti	323.904	Be	205.590	Ho	348.484
W	207.911	Sn	189.989	La	333.749
Mg	279.553	P	213.618	Nd	430.357
Al	309.284	Ba	455.403	Sc	365.180
V	268.796	K	766.490	Sm	359.260
Cr	283.563	Na	589.592	Tb	350.917
Mn	260.569	Sb	206.833	Tm	346.220
Co	238.892	Sr	215.284	Lu	261.542
Cu	213.598	Zn	213.856	Yb	369.420
Bi	222.825	Y	360.072	Pr	406.282

3. Results and Discussion

3.1 Effect of niobium matrix concentration on analyte determinations

With its line rich emission spectra, niobium interferes with most of the elements and some of the elements have enhanced background levels in presence of niobium matrix. To study the effect of Nb matrix on elemental sensitivities, S/B was calculated at different matrix concentrations levels of 1mg/ml, 5mg/ml, 10mg/ml and were compared with the S/B obtained without matrix. These findings are shown in bar chart in **Fig. 2**.

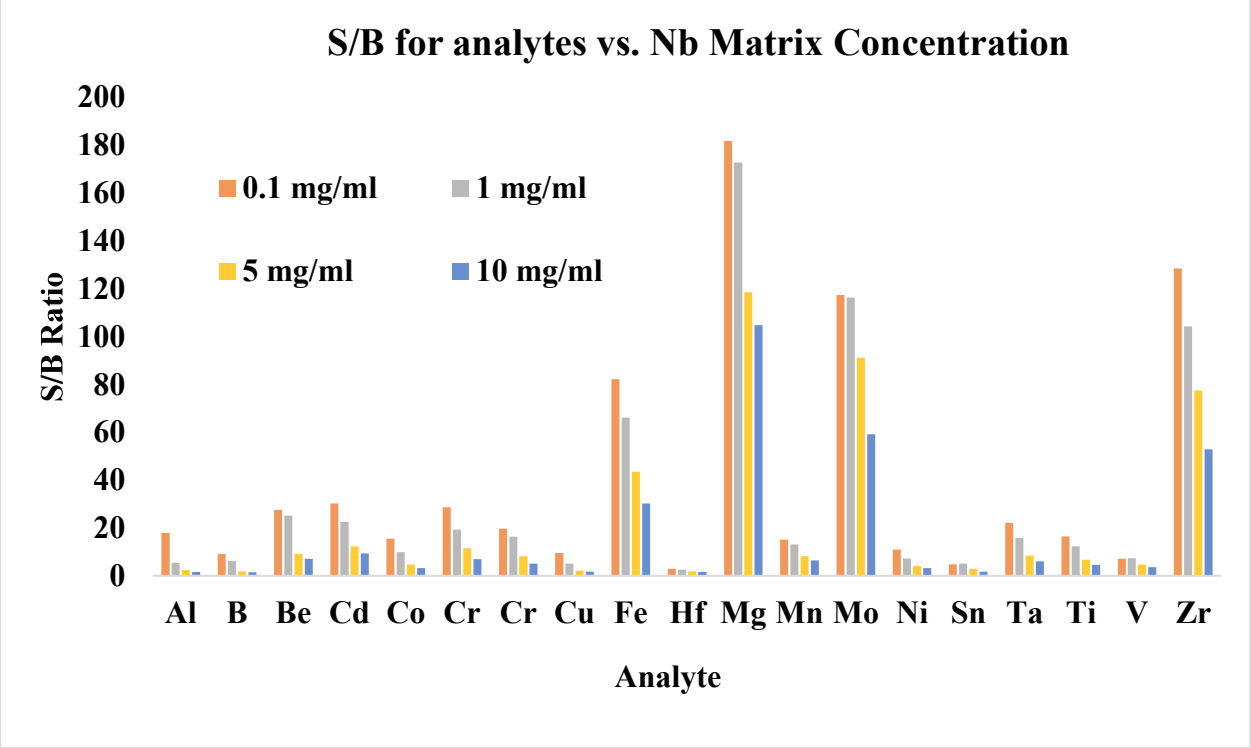

Fig. 2. Effect on S/B ratio for analytes with variation in Nb Matrix Concentration

It can be seen from the above figure that niobium matrix with its concentration above 5mg/ml has strong effect on the S/B ratio of analytes which severely affects the detection limits for impurities. If matrix concentration is diluted below 5mg/ml, it dilutes the impurities as well, which in turn could impact their detection limits. Hence, 5mg/ml matrix concentration was chosen as optimum matrix concentration in the present method. From the above bar chart, elements are segregated into two groups. The elements which show the decrease of greater than 10% per 1mg/ml in S/B ratio as severely affected group of elements, namely Al, Cd, Co, Cr, Cu, Ni, Ti. The second group of elements which show a

decrease of less than 10% per 1mg/ml in S/B ratio as less effected group of elements, namely Fe, Hf, Mg, Mn, Mo, Sn, V, Zr.

3.2 Optimization of ICP-OES Instrumental Parameters

For Optimization of ICP plasma parameters, Fe 238.204 nm line was taken. With increase in forward RF power of the source, it is seen that there is an increase in signal intensity and average background intensity. At 1000 W R.F. Power, S/B was found to be maximum, which decreased subsequently. So 1000 W was selected as optimum power for this method. Plasma gas flow rate of 12 L/min and nebulizer gas flow rate of 0.9 L/min found to be optimum for the method.

3.3 Analytical Range

Using optimized conditions, instrument was calibrated using standards containing all analytes at various concentration levels of interest. All the calibration plots were found to be linear with correlation coefficient greater than 0.99 having analytical range to be as shown in Table 2.

3.4 Limits of detection

The Limits of detection (LOD) were calculated using the following formula outlined in reference[10] and are summarized in Table 4A & 4B.

LOD = Background Equivalent Concentration (BEC) X 0.03;

BEC = I_b / (I_p-I_b) * concentration of element (µg/ml) * dilution factor (ml/gm)

I_b = average background intensity for element of interest

I_p = Peak intensity of element of interest

Table 4A Limits of detection for analytes in niobium matrix vs. Specification limits for RRR-Nb

Element	LOD (ppm)	Specification Limits for RRR-Nb (ppm)	Element	LOD (ppm)	Specification Limits for RRR-Nb (ppm)
Fe	< 5	< 30	V	< 3	< 30
Mo	< 3	< 50	Cr	< 5	< 30
Ni	< 8	< 30	Mn	< 3	< 30
Si	< 5	< 30	Co	< 10	< 30
Ta	< 15	< 500	Cu	< 6	< 30
Ti	< 2	< 40	Zr	< 3	< 30
W	< 15	< 70	Cd	< 2	< 30

Mg	< 2	< 30	Hf	< 3	< 30
Al	< 6	< 30	Pb	< 6	< 30

Table 4B Limits of detection for analytes in niobium matrix

Element	LOD (ppm)	Element	LOD (ppm)	Element	LOD (ppm)
B	< 2	La	< 5	Na	< 15
Be	< 10	Nd	< 10	Sb	< 15
Y	< 2	Sc	< 10	Sr	< 15
Ce	< 10	Sm	< 5	Zn	< 5
Dy	< 2	Yb	< 2	Bi	< 15
Er	< 5	Pr	< 5	Sn	< 10
Eu	< 2	Tm	< 2	Ba	< 2
Gd	< 5	Lu	< 2	K	< 25
Ho	< 10	Tb	< 10		

3.5 ICP-OES Analysis of Spiked Samples

In order to validate the method, the standard recovery was monitored by spiking real time samples of Niobium metal and the recovery values were found to be between 100 ± 10% which is shown in Table 5. This shows the reliability of the method developed.

Table 5 ICP-OES Standard recovery results for spiked analytes in Niobium Matrix

Element	Amount Spiked (µg/ml)	Amount Observed (µg/ml)	% Recovery	Element	Amount Spiked (µg/ml)	Amount Observed (µg/ml)	% Recovery
Al	2	2	100	Ta	5	5.095	101.9
B	0.5	0.48	96	Ti	1	0.985	98.5
Be	1	1	100	V	1	1	100
Cd	0.5	0.5	100	Zr	5	4.96	99.1
Co	1	0.975	97.5	W	2	2.02	101
Cr	1	0.995	99.5	Si	2	2.00	100
Cu	1	0.91	91	Pb	2	2.02	101
Fe	5	5.075	101.5	P	2	2.01	100.5
Hf	2	1.82	91	Ba	1	1.00	100

Mg	1	0.975	97.5	K	1	1.05	105
Mn	2	2	100	Na	1	0.96	96
Mo	1	0.985	98.5	Sb	1	0.95	95
Ni	1	1.015	101.5	Sr	1	0.99	99
Sn	1	1.015	101.5	Zn	1	1.01	101
Ta	5	5.095	101.9	Bi	1	1.05	105
Ti	1	0.985	98.5	REE	1	0.98-1.02	98-102

3.6 ICP-OES Analysis Results for Real-Time Samples

Typical samples each from high pure Nb_2O_5, pure Nb metal are analyzed and the results obtained along with % RSD are given in Table 6. % RSD found to be better than 3% for all the elements of interest. Concentration for all REEs is found to be below detection limits (BDL) and hence not given here**.**

Table 6 Analysis results pertaining to real time samples

Element	**Nb_2O_5 (ppm)**	**Pure Nb (ppm)**	**Element**	**Nb_2O_5 (ppm)**	**Pure Nb (ppm)**
Al	43	< 20	Ti	< 6	< 6
B	< 5	< 5	V	< 10	< 10
Be	< 10	< 10	Zr	100	35
Cd	< 5	< 5	W	105	71
Co	< 30	< 30	Si	59	< 15
Cr	< 15	< 15	Pb	< 20	< 20
Cu	< 20	< 20	P	< 10	< 10
Fe	75	< 15	Ba	< 6	< 6
Hf	< 10	< 10	K	< 75	< 75
Mg	26	< 6	Na	< 50	< 50
Mn	< 10	< 10	Sb	< 50	< 50
Mo	< 10	< 10	Sr	< 50	< 50
Ni	< 25	< 25	Zn	< 15	< 15
Sn	< 30	< 30	Bi	< 50	< 50
Ta	352	101	REE	< DL	< DL

Conclusion

The developed method facilitates rapid analysis of high pure niobium oxide and niobium metal as it does not require prior separation of matrix. It enables high sample throughput which is the main requirement for an industrial laboratory where sample load is high and timely reporting of results is mandatory to meet the production schedules. This method is routinely used for clearing real time production samples.

Conflicts of Interest:

Authors of this manuscript stating that "there are no conflicts to declare"

Author contributions:

Y Balaji Rao: Conceptualization; Methodology; Formal analysis; Data curation; Validation, Writing-original draft, Review & Revisions and editing

P V Nagendra Kumar: Supervision, conceptualization, resources, writing-review and editing

S NVMS Gupta: Helping in experiments, Review & Revisions and editing

Dinesh Srivastava: Supervision, conceptualization, resources, writing-review and editing

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