Development of ICP-AES-based Methodology for the Determination of Trace Metallic Constituents in Zr-Nb Alloy

Sunita Pathak and Arijit Sengupta*

Radiochemistry Division, Bhabha Atomic Research Centre,
Mumbai, India

INTRODUCTION

Due to the advantageous properties such as low neutron absorption cross-section, high mechanical strength, good irradiation stability, and corrosion resistance, Zr-based alloy materials are being extensively used as cladding and structural materials for nuclear fuel materials (1-5). Zircaloy-4 alloy has been used as cladding material for several years in the pressurized water reactor without any significant problem. To fulfill the energy demand, advanced Zr-based alloys are now being required for the drastic operating conditions such as higher burn-up, increased operating temperature, and high pH operation. Several new Zr-based alloy materials such as Zr-1.0Nb-1.0Sn-0.1Fe, Zr-1Nb-O, and Zr-0.1Nb-1.0Sn-0.27Fe-0.16Cr were synthesized, characterized, and tested in nuclear reactors (6-10), and the Zr-Nb alloy showed very promising properties. The metallurgical properties and the performance of such nuclear materials depends largely on the concomitant metal ions present in the alloy (11-14). Therefore, a stringent chemical quality control is required to get its desired performance. In this manuscript, an ICP-AES-based method was developed for the determination of metallic constituents at the trace level in a Zr-Nb matrix.

ICP-AES, being a simultaneously multi-elemental and reliable technique with desirable analytical performance including detection limit, sensitivity, linear dynamic range,

ABSTRACT

A simple methodology was developed for the determination of trace metallic constituents (Ag, B, Ba, Bi, Ca, Cd, Ce, Ga, Gd, In, K, La, Li, Lu, Mg, Mn, Na, Co, Cr, Cu, Dy, Eu, Fe, Nd, Ni, Pb, Pr, Sm, Sr, Tl, and Zn) in Zr-Nb alloy. The systematic study of the spectral interference of Zr as well as Nb was carried out on these analytes. This includes identification of interference-free lines, tolerance level, and correction factors associated with each line. The analytical performance of these lines including detection limit, sensitivity, and linear dynamic range was also investigated. Based on these two factors, the best line of each analyte was chosen. Chemical separation of the major matrix followed by the analysis of the raffinate was the strategy adopted in the development of the method. To optimize the chemical separation procedure, TBP, TOPO, and DHOA were used for preferential separation of the major matrix without loss of the analytes even at trace levels. The optimized method was validated using a synthetic sample, which revealed that five contacts of 1.1 M TBP in dodecane was the ideal choice for separation and all of these analytes can be determined at the 1-mg L^{-1} level in a Zr-Nb matrix with a RSD less than 5%.

and precision, is routinely employed for the determination of trace metallic constituents in different nuclear materials (15-20). Due to the high excitation temperature of the plasma, more emission lines are available for the determination but some may lead to spectral interference. Mainly the nuclear material

matrix elements are multi-electronic and have emission-rich spectra; hence, they are expected to show severe spectral interference while determining the analytes in these matrices especially at the trace level (21-25). Therefore, either incorporation of correction factors for spectral interference or chemical separation of the major matrix are the two strategies adopted in an ICP-AES-based methodology. The first option leads to a situation where the detection limit becomes poorer than the aqueous matrix, while the second option requires a suitable extractant which can preferentially separate the targeted emission-rich metal ion without extracting the analytes of interest even at the trace level. TBP (tri-n-butyl phosphate), DHOA (di-n-hexyl octanamide), and TOPO (tri-n-octyl phosphate) were employed in the different stages of the nuclear fuel cycles, including its analytical application in trace metal assay of different nuclear material matrices (26-30). In the present case, a comparative study was carried out using these ligands to optimize the procedure: the aqueous feed acidity, the number of contacts required for separation of Zr as well as Nb, and whether there is any loss of the analytes even at the trace level during the chemical separation of the major matrix.

EXPERIMENTAL

Instrumentation

The methodology was developed on a simultaneous multi-elemental inductively coupled plasma atomic emission spectrometer (Spectro-Arcos, Germany) with a high-performing charge-coupled device (CCD) as the detector. The

*Corresponding author.
E-mail: arijita@barc.gov.in

optimized instrumental parameters are summarized elsewhere (31) and in Table I.

Standard Solutions and Reagents

Standard solutions for all of the analytes were prepared from CertiPUR® ICP multi-standard solutions (E-Merck, Darmstadt, Germany) by proper dilution. Suprapur® HNO₃ (E-Merck) and quartz double-distilled water were used throughout the investigation. Multi-point standardization was carried out using 0.5 M HNO₃ as a lower standard and 0.05–1000 mg/L of the corresponding elemental standard as the higher standards for establishing calibration curves for all the analytes. All measurements were done in five replicates. TBP and TOPO were procured from Koch-

Light Laboratories and Cytec Industries, Inc., USA. DHOA was synthesized by a previously reported method (32).

Procedure

During the spectral interference study, CertiPUR® Zr and Nb solutions at different concentrations were fed to the plasma as the samples and the contribution in each analytical lines were monitored. The interference was found to vary linearly with the concentration of interfering ion and hence, the correction factors were calculated accordingly. The tolerance level of the interfering element was chosen as the maximum level of concentration of that element beyond which a particular line of analyte is interfered.

Preparation of Synthetic Samples

The synthetic samples were prepared by addition of suitable aliquots of the corresponding analytes from their individual CertiPUR® solutions. The acidity of the aqueous feed of the synthetic solution used for the ICP-AES analysis was kept at 3 M HNO₃ as optimized from the procedure.

RESULTS AND DISCUSSION

Analytical Performance of Different Emission Lines of the Analytes

Due to the high excitation energy of the plasma, different levels of electronic excitation take place in the analytes which leads to a large number of emission lines in the spectra. Not any emission line can be taken as an analytical line. Different merits of the analytical performance need to be investigated before choosing an emission line as the analytical lines of the elements. The most promising characteristic for an analytical line is that the response with respect to concentration should vary linearly at a sufficient length of the concentration range which is a prerequisite for the determination of the analytes. Table II summarizes the analytical performance of different lines of the analytes in aqueous medium. The data reported were on the basis of 10 replicate readings. The detection limit calculated as the concentration corresponding to the intensity equal to the average of blank values + three time of the standard deviation of the blank. The sensitivity was evaluated as the slope of the calibration curves established, while the linear dynamic range is the concentration range where the concentration and the response varies linearly. The line for each element with lowest detection limit, large linear dynamic range, high value of sensitivity, and best analytical performance is as follows: Ag 328.068 nm, Al 396.152 nm,

TABLE I
Specifications And Operating Conditions Of ICP-AES

Instrumental Specifications	
Model No.	Arcos FH12 ICP-AES
Optical design	Paschen-Runge mounting, Circular design
Focal length	750 mm
Grating	Holographic
Groove density	1800 grooves/mm (1), 3600 grooves/mm (2)
Wavelength range	130-800 nm
Entrance slit width	15 microns
Resolution (FWHM)	0.01 nm from 130-450 nm 0.02 nm from 450-800 nm
Thermal regulation	Controlled to 30 ± 1 °C
Frequency	27.12 MHz
Pump	Dual channel peristaltic pump
Detector	Linear arrays of CCD (3648 pixels/array)
Nebulizer	Concentric nebulizer with cyclonic spray chamber
ICP-torch	Demountable, radial viewing
Operating Conditions	
Coolant flow	16 L/min
Auxiliary flow	0.7 L/min
Total time of measurement	30 s
Pump speed	25 rpm
RF power out put	1.0 kW
Input power	230 V AC

TABLE II
Analytical Performance of Different Analytical Lines of Common Metallic Constituents and REEs

	Analytical Line	Linear Dynamic Range (mg/L)	DL (mg/L)	Sensitivity		Analytical Line	Linear Dynamic Range (mg/L)	DL (mg/L)	Sensitivity
Ag	224.641	4.77 - 1200	4.76	132.1	Ga	141.444	12.3-1200	12.3	8.3
	243.779	0.162-1200	0.162	4727.6		287.424	6.19-1200	6.19	107.6
	328.068	0.022-1200	0.022	13295.1		294.364	1.25-1200	1.25	861.2
	338.289	0.0367-1200	0.0367	8306.8		417.206	0.015-1200	0.015	20707.4
Al	167.078	4.39- 1200	4.39	16.2	Gd	335.047	0.0235-2400	0.0235	28915.8
	176.641	4.57-1200	4.57	8.8		335.862	0.0387-2400	0.0387	10967.7
	308.215	0.237-1200	0.237	1156.1		336.223	0.0178-2400	0.0178	17967.6
	309.271	0.0329-1200	0.0329	8102.8		342.247	0.0116-2400	0.0116	231975.4
B	394.401	0.017-1200	0.017	20100.2	In	230.606	1.73-1200	1.73	375.5
	396.152	0.0104-1200	0.0104	37055.2		303.936	2.47-1200	2.47	500.4
	136.246	9.25-1200	9.25	9.7		325.609	1.53-1200	1.53	896.7
	182.641	0.294-1200	0.294	1295		451.131	0.409-1200	0.409	497.8
Ba	208.959	0.141-1200	0.141	1784.8	K	404.721	1.51-1200	1.51	167.4
	249.667	0.476-1200	0.476	1151		766.461	0.149-1200	0.149	1191.4
	249.773	0.238-1200	0.238	2415.3		333.749	0.0106-2400	0.0106	82356.8
	230.424	0.157-1200	0.157	4959.7		379.478	0.0056-2400	0.00084	549601.4
Bi	233.527	0.167-1200	0.167	3849.1	La	408.672	0.0106-2400	0.000329	436094.1
	455.404	0.018-1200	0.018	105554.5		274.118	1.5 -1200	15	37.3
	143.683	5.24- 1200	5.24	9.1		323.261	3.79-1200	3.79	206.2
	153.317	8.97-1200	8.97	8.6		460.289	1.85-1200	1.85	540.5
Ca	190.241	4.67-1200	4.67	84.1	Li	670.780	0.00214-1200	0.00214	135567.3
	206.17	0.0281-1200	0.0281	41803.2		219.554	2.58-2400	2.58	380.4
	222.825	4.58-1200	4.58	115.7		261.542	1.49-2400	1.49	977.2
	223.061	3.89-1200	3.89	140.3		291.139	2.13-2400	2.13	711.8
Cd	306.772	2.71-1200	2.71	423.6	Lu	307.76	0.259-2400	0.259	2667.8
	183.801	1.61-1200	1.61	101.8		202.647	0.651-1200	0.651	496.2
	393.366	0.0187-1200	0.0187	12376292		279.079	2.42-1200	2.42	214.9
	396.847	0.0179-1200	0.0179	5947582		279.553	0.00754-1200	0.00754	65145.1
Ce	422.673	0.0184-1200	0.0184	65217.8	Mg	280.27	0.00738-1200	0.00738	42245.9
	214.438	0.0551-1200	0.0551	7356.4		285.213	0.156-1200	0.156	5103.2
	226.502	0.0846-1200	0.0846	4707.8		257.611	0.0555-1200	0.0555	14383.2
	228.802	0.239-1200	0.239	3330.4		259.373	0.0672-1200	0.0672	11850.7
Co	361.051	0.0682-1200	0.0682	2712.7	Mn	260.569	0.0844-1200	0.0844	8907.7
	393.373	0.364-2400	0.364	1084913		294.921	0.133-1200	0.133	9945.5
	413.38	0.0023-2400	0.0023	95132.2		403.076	0.0613-1200	0.0613	11988.8
	413.765	0.0079-2400	0.0079	86539.8		330.237	0.0277-1200	0.0277	1761.4
Cu	418.66	0.0042-2400	0.0042	95637.4	Na	330.298	1.3 -1200	1.3	239.5
	448.691	0.116-2400	0.116	5431.6		588.995	0.0381 -1200	0.0381	55535.3

Table II cont'd.

TABLE II (cont'd)
Analytical Performance of Different Analytical Lines of Common Metallic Constituents and REEs

	Analytical Line	Linear Dynamic Range (mg/L)	DL (mg/L)	Sensitivity		Analytical Line	Linear Dynamic Range (mg/L)	DL (mg/L)	Sensitivity
Co	228.616	0.326-1200	0.326	2587.6	Nd	401.225	0.0265-2400	0.0265	110796
	230.786	0.348-1200	0.348	2123.1		406.109	0.00466-2400	0.00466	108292.9
	237.862	0.727-1200	0.727	909.9		417.731	0.0147-2400	0.0147	48009.1
	238.892	0.494-1200	0.494	1468.4		430.358	0.00821-2400	0.00821	112295.8
Cr	205.618	0.024-1200	0.024	18014.5	Ni	174.828	6.72 -1200	6.72	19.3
	267.716	0.246-1200	0.246	1789.9		221.648	1.28 -1200	1.28	1021
	283.563	0.197-1200	0.197	3667.2		227.021	1.73 -1200	1.73	60.6
	284.325	0.458-1200	0.458	1724.2		231.604	0.27-1200	0.27	2035.9
Cu	284.984	0.595-1200	0.595	1074.6	Pb	232.003	0.807-1200	0.807	896.3
	219.226	0.89-1200	0.89	501.6		300.249	0.84 -1200	0.84	1851
	219.958	0.036-1200	0.036	13916.7		341.476	0.1 -1200	0.1	14391.2
	224.7	0.759-1200	0.759	762.3		167.153	4.97-1200	4.97	17.6
Dy	324.754	0.0787-1200	0.0787	17220.1	Pr	168.215	6.92 -1200	6.92	17.4
	327.396	0.0255-1200	0.0255	14780.8		172.68	6.05 -1200	6.05	16.9
	340.78	0.00164-2400	0.00164	121163.9		220.353	12.6 -1200	12.6	31.7
	353.17	0.00135-2400	0.00135	548458.6		261.418	0.285 -1200	0.285	2080.5
Eu	353.602	0.0029-2400	0.0029	149494.8	Sm	283.305	8.15 -1200	8.15	87.4
	364.54	0.0026-2400	0.0026	220814.9		405.778	0.222 -1200	0.222	2362.1
	394.468	0.00529-2400	0.00529	176839.9		411.846	0.0033- 2400	0.0033	312419.6
	381.967	0.000702-2400	0.000702	1606502		414.311	0.000994-2400	0.000994	4311280
Fe	390.71	0.000871-2400	0.000871	675848.3	Sr	417.939	0.00147-2400	0.00147	412745.4
	393.048	0.000739-2400	0.000739	869738.7		422.535	0.00102-2400	0.00102	514045.8
	420.505	0.000575-2400	0.000575	1114643		359.26	0.00112-2400	0.00112	119619.4
	238.204	0.451-1200	0.451	2114.9		360.428	0.00129-2400	0.00129	44879.5
	239.562	0.423-1200	0.423	1906.5	Tl	428.079	0.00797-2400	0.00797	97725.2
	241.331	2.86-1200	2.86	250.9		442.434	0.0123-2400	0.0123	99263.8
	244.451	10-20000	10	59.4		407.771	0.000506 - 1200	0.000506	6548966
	259.941	0.388-1200	0.388	2568.6		421.552	0.000573 -1200	0.000573	3885036
	261.187	0.779-1200	0.779	992.6	Zn	460.733	0.0966 -1200	0.0966	10825.2
	262.567	2.34-1200	2.34	292.9		132.171	11.5- 1200	11.5	8
	262.829	2.54-1200	2.54	277.8		190.864	0.793 -1200	0.793	258.1
	275.573	1.39-1200	1.39	329.1		276.787	7.08 -1200	7.08	67.2
	373.486	0.0118-1200	0.0118	7034.4		202.613	0.0733 -1200	0.0733	5463.2
	589.592	0.0482-1200	0.0482	26193.5		206.2	0.144 -1200	0.144	2080.4
						213.856	0.0489 -1200	0.0489	5959.8
						334.502	0.471 -1200	0.471	745.9

B 249.773 nm, Ba 455.404 nm, Bi 206.170 nm, Cd 214.438 nm, Fe 373.486 nm, Nd 406.109 nm, Ni 341.476 nm, Pb 405.778 nm, K 766.461 nm, Li 670.780 nm, Dy 353.170 nm, Sm 359.260 nm, Lu 307.760 nm, Mg 279.553 nm, Sr 407.771 nm, Mn 257.611 nm, Tl 190.864 nm, Zn 213.856 nm, Co 228.616 nm, Cr 205.618 nm, Cu 327.396 nm, Pr 414.311 nm, Gd 342.247 nm, and Eu 381.967.

The Ca 396.847-nm line showed the lowest detection limit, while the 393.366-nm line was the most sensitive. Comparing both of these lines, Ca 393.366 nm was found to be the best with a detection limit of 0.0187 mg L⁻¹ and sensitivity of 12376292. The Ce 413.380 nm, 413.765 nm, and 418.660 nm lines were found to have very good analytical performance, but the 413.380 nm line was found to be the best. The La 408.672-nm line showed lowest detection limits, while the La 379.478-nm line is the most sensitive. Any of these two lines can be chosen for its determination. Though the Na 330.237-nm line showed lower detection limit than Na 588.995 nm, the latter is more than 50 times more sensitive and hence, was chosen for its analysis.

Spectral Interference

Although the presence of the additional emission lines in ICP enhances the option of choosing additional analytical lines for the determination of analytes, yet it causes severe spectral interferences. Mainly, the multi-electronic elements such as Zr and Nb are expected to interfere during the determination of analytes, especially at trace level. Hence, it leads to erroneous results of the trace metal assay. There are basically two methodologies that can solve this issue. First, the emission-rich matrices can be preferentially removed without loss of analyte even at trace level or, second, per-

form a systematic study of spectral interference of Zr and Nb and apply the correction factors where necessary. The first option requires a selective extractant and more sample handling, while the second option may not be sufficient for very low level determinations.

Interference From Zr

The interference study includes identification of the interference-free analytical line for the analytes, evaluation of the tolerance level of the emission-rich matrix, and determination of the correction factor for each line. Table III summarizes the parameters on the spectral interference of Zr on different analytes: Na 589.529 nm, Na 588.995 nm, Mg 202.647 nm, K 766.491 nm, Ca 396.847 nm, Ca 183.801 nm, Bi 206.170 nm, Ce 413.765 nm, B 182.641 nm, B 208.959 nm, Ni 221.648 nm, Zn 213.856 nm, and Pr 411.846 nm lines were found to have no spectral interference from Zr. The Cr 205.618 nm, Mn 259.373 nm, Fe 238.204 nm, Tl 190.864 nm, Al 394.401 nm, Sr 460.733 nm, Ba 233.527 nm, Cu 324.754 nm, Li 670.780 nm, Co 228.616 nm, Ag 243.779 nm, Lu 307.760 nm, Ga 417.206 nm, La 408.672 nm, Nd 417.731 nm, and Eu 390.710 nm analytical lines were found to be least interfered by Zr matrix with the tolerance level 500 mg L⁻¹, 100 mg L⁻¹, 100 mg L⁻¹, 500 mg L⁻¹, 100 mg L⁻¹, 500 mg L⁻¹, 100 mg L⁻¹, 100 mg L⁻¹, 500 mg L⁻¹, 100 mg L⁻¹, 100 mg L⁻¹, 500 mg L⁻¹, 500 mg L⁻¹, 500 mg L⁻¹ and 500 mg L⁻¹, respectively. Analytes like Pb (405.778 nm, 261.418 nm), Cd (214.438 nm, 226.502 nm), In (230.606 nm, 451.131 nm), Sm (359.260 nm, 442.434 nm) and Dy (353.170 nm, 364.540 nm) showed more than one line having least interference from Zr with the tolerance level of 100 mg L⁻¹.

Interference from Nb

Since only 10–20% of Nb is present in the Zr-Nb alloy, the spectral

interference of Nb will not be as prominent as Zr. A systematic study of the spectral interference of Nb on other analytical wavelengths of the elements was carried out (see Table IV). The following had no interference from Nb: Na (589.592 and 588.995 nm), K (766.491 and 404.721 nm), Ca (393.366 nm and 183.801 nm), Cr (205.618 nm), Fe (262.567 nm and 373.486 nm), B (249.773 nm and 182.641 nm), Al (176.641 nm), Tl (190.864 nm), Sr (421.552 nm and 460.733 nm), Bi (190.241 nm, 222.825 nm, and 206.170 nm), Li (670.780 nm), Co (228.616 nm, 230.786 nm, and 237.862 nm), Ni (231.604 nm, 221.648 nm, and 341.476 nm), Zn (213.856 nm and 206.200 nm), Ag (328.068 nm), Cd (361.051 nm), Ga (417.206 nm), In (230.606 nm, 451.131 nm, 460.289 nm, and 323.261 nm), La (408.672 nm, 333.749 nm, and 374.478 nm), Ce (418.660 nm, 448.691 nm, 413.380 nm, 393.373 nm), Pr (411.846 nm, 417.939 nm, and 422.535 nm), Nd (430.358 nm, 417.731 nm), Sm (359.260 nm, 442.434 nm, 428.079 nm, and 360.428 nm), Eu (381.967 nm, 393.048 nm, 390.710 nm) and Dy (353.170 nm, 394.468 nm). For other analytes, the least interfered lines were identified along with their tolerance level and correction factors. The analytical lines of Mn 260.569 nm, Pb 405.778 nm, Cu 327.396 nm, Gd 335.047 nm, and Lu 361.542 nm were found to show the least interference from Nb with a tolerance level of 500 mg L⁻¹ for all except Cu at 327.396 nm (tolerance of Nb 200 mg L⁻¹).

The overall study revealed that, comparatively, the spectral interference of Zr showed a more pronounced effect during the analysis of the trace metals. Therefore, it is a prerequisite to separate Zr preferentially without any loss of the analytes even at the trace level.

TABLE III
Spectral Interference of Zr on Different Analytical Lines of the Elements

	Analytical Line (nm)	Contri- bution From 1000 ppm Zr	Toler- ance Level (mg/L)	Correction Factor		Analytical Line (nm)	Contri- bution From 1000 ppm Zr	Toler- ance Level (mg/L)	Correction Factor
Na	589.592	BDL	1000	NO INTERFERENCE	B	249.773	7.605	0.5	0.007605
	588.995	BDL	1000	NO INTERFERENCE		249.677	22.222	1	0.022222
	330.237	96.512	0.05	0.096512		182.641	BDL	1000	NO INTERFERENCE
	330.298	436.878	20	0.436878		208.959	BDL	1000	NO INTERFERENCE
Mg	279.553	0.462	0.05	0.000462	Al	136.246	394.428	20	0.394428
	280.27	0.459	0.05	0.000459		167.078	361.303	20	0.361303
	285.213	71.633	0.05	0.071633		396.152	57.081	1	0.057081
	279.079	85.762	100	0.085762		394.401	1.29	100	0.00129
K	202.647	BDL	1000	NO INTERFERENCE	Ti	176.641	325.454	50	0.325454
	766.491	BDL	1000	NO INTERFERENCE		308.215	17.019	100	0.017019
	404.721	551.068	20	0.551068		309.271	6.273	1	0.006273
						190.864	3.566	500	0.003566
Ca	396.847	BDL	1000	NO INTERFERENCE	Sr	132.171	459.833	20	0.459833
	393.366	0.039	500	0.000039		276.787	253.539	50	0.253539
	183.801	BDL	1000	NO INTERFERENCE		407.771	0.003	100	0.000003
	422.673	0.826	10	0.000826		421.552	0.039	100	0.000039
Cr	267.716	14.87	100	0.01487	Ba	460.733	0.135	500	0.000135
	205.618	0.068	500	0.000068		455.404	0.538	50	0.000538
	283.563	97.01	1	0.09701		233.527	1.221	100	0.001221
	284.325	81.506	0.05	0.081506		230.424	3.02	100	0.00302
Mn	284.984	39.206	100	0.039206	Bi	223.061	21.43	500	0.02143
	257.611	3.998	20	0.003998		190.241	136.809	100	0.136809
	259.373	1.577	100	0.001577		306.772	158.407	0.05	0.158407
	260.569	4.912	100	0.004912		222.825	8.139	500	0.008139
Fe	294.921	26.509	10	0.026509	Pb	153.317	404.799	50	0.404799
	403.076	10.351	20	0.010351		143.683	388.723	20	0.388723
	259.941	4.448	10	0.004448		206.17	BDL	1000	NO INTERFERENCE
	238.204	5.264	100	0.005264		220.353	112.962	100	0.112962
	239.562	4.81	10	0.00481		168.215	345.695	20	0.345695
	244.451	385.825	100	0.385825					

TABLE III (cont'd.)

TABLE III (cont'd.)
Spectral Interference of Zr on Different Analytical Lines of The Elements

	Analytical Line (nm)	Contri- bution From 1000 ppm Zr	Toler- ance Level (mg/L)	Correction Factor		Analytical Line (nm)	Contri- bution From 1000 ppm Zr	Toler- ance Level (mg/L)	Correction Factor
Fe	261.187	15.177	10	0.015177	Pb	167.153	335.923	20	0.335923
	262.567	26.534	100	0.026534		172.68	359.134	20	0.359134
	262.829	41.608	100	0.041608		405.778	3.321	100	0.003321
	275.573	36.526	50	0.036526		283.305	148.822	100	0.148822
	241.331	31.081	100	0.031081		261.418	3.768	100	0.003768
	373.486	3.301	100	0.003301	Li	670.78	0.019	100	0.000019
Co	228.616	1.739	500	0.001739		460.289	76.117	100	0.076117
	238.892	10.867	100	0.010867		323.261	214.029	20	0.214029
	230.786	2.856	100	0.002856		274.118	2161.41	10	2.16141
	237.862	84.807	20	0.084807	La	408.672	0.014	500	0.000014
Ni	231.604	5.689	100	0.005689		333.749	3.238	20	0.003238
	221.648	BDL	1000	NO INTERFERENCE		379.478	0.047	100	0.000047
	232.003	8.714	100	0.008714	Ce	418.66	256.962	1	0.256962
	227.021	38.182	100	0.038182		448.691	6.831	100	0.006831
	174.828	374.178	20	0.374178		413.38	BDL	1000	NO INTERFERENCE
	300.249	12.387	100	0.012387		413.38	1.627	100	0.001627
Cu	341.476	174.381	0.1	0.174381	Pr	393.373	1.177	100	0.001177
	324.754	0.962	100	0.000962		411.846	BDL	1000	NO INTERFERENCE
	327.396	23.038	5	0.023038		417.939	1.031	100	0.001031
	224.7	7.952	100	0.007952		422.535	0.584	20	0.000584
	219.226	8.732	100	0.008732	Nd	414.311	0.218	100	0.000218
	219.958	1.738	100	0.001738		401.225	10.57	10	0.01057
Zn	213.856	BDL	1000	NO INTERFERENCE		430.358	0.253	100	0.000253
	206.2	0.578	500	0.000578		406.109	0.323	100	0.000323
	202.613	0.454	100	0.000454	Sm	417.731	0.188	500	0.000188
	334.502	704.9	1	0.7049		359.26	0.197	100	0.000197
Ag	328.068	414.093	0.5	0.414093		442.434	0.148	100	0.000148
	338.289	4.256	50	0.004256		428.079	0.295	100	0.000295
Cd	224.641	61.563	100	0.061563	Eu	360.428	0.959	100	0.000959
	243.779	1.701	100	0.001701		420.505	0.029	100	0.000029
	214.438	1.024	100	0.001024		381.967	0.365	100	0.000365
	226.502	1.134	100	0.001134		393.048	0.052	100	0.000052
Ga	228.802	2.09	100	0.00209	Gd	390.71	0.004	500	0.000004
	361.051	40.852	20	0.040852		342.247	0.276	100	0.000276
	141.444	419.055	50	0.419055		335.047	47.552	1	0.047552
	417.206	0.147	500	0.000147		336.223	8.38	0.05	0.00838
In	294.364	22.834	100	0.022834	Dy	335.862	13.839	20	0.013839
	287.424	324.653	50	0.324653		353.17	0.073	100	0.000073
	230.606	14.581	100	0.014581		394.468	0.16	100	0.00016
	325.609	143.989	20	0.143989		340.78	14.05	1	0.01405
	451.131	11.426	100	0.011426	Lu	353.602	1.79	20	0.00179
	303.936	253.123	20	0.253123		364.54	0.083	100	0.000083
						261.542	59.116	50	0.059116
						291.139	36.806	100	0.036806
						307.76	8.752	100	0.008752
						219.554	17.99	100	0.01799

TABLE IV
Spectral Interference of Nb on Different Analytical Lines of the Elements

	Analytical Line (nm)	Contri- bution From 1000 ppm Nb	Toler- ance Level (mg/L)	Correction Factor		Analytical Line (nm)	Contri- bution From 1000 ppm Nb	Toler- ance Level (mg/L)	Correction Factor
Na	589.592	BDL	1000	NO INTERFERENCE	B	249.773	BDL	1000	NO INTERFERENCE
	588.995	BDL	1000	NO INTERFERENCE		249.677	16.782	100	0.016782
	330.237	6.095	0.05	0.006095		182.641	BDL	1000	NO INTERFERENCE
	330.298	32.849	100	0.032849		208.959	1.237	100	0.001237
Mg	279.553	1.085	0.05	0.001085	Al	136.246	30.359	500	0.030359
	280.27	1.652	0.05	0.001652		167.078	15.692	500	0.015692
	285.213	1.287	0.1	0.001287		396.152	1.554	50	0.001554
	279.079	268.903	20	0.268903		394.401	0.077	500	0.000077
K	202.647	BDL	1000	NO INTERFERENCE	Ti	176.641	BDL	1000	NO INTERFERENCE
	766.491	BDL	1000	NO INTERFERENCE		308.215	4.896	50	0.004896
	404.721	BDL	1000	NO INTERFERENCE		309.271	6.148	1	0.006148
	396.847	0.069	0.1	0.000069		190.864	BDL	1000	NO INTERFERENCE
Ca	393.366	BDL	1000	NO INTERFERENCE	Sr	132.171	45.262	100	0.045262
	183.801	BDL	1000	NO INTERFERENCE		276.787	1534.79	20	1.53479
	422.673	0.06	0.1	0.00006		407.771	0.005	50	0.000005
	267.716	0.881	500	0.000881		421.552	BDL	1000	NO INTERFERENCE
Cr	205.618	BDL	1000	NO INTERFERENCE	Ba	460.733	BDL	1000	NO INTERFERENCE
	283.563	0.67	500	0.00067		455.404	BDL	1000	NO INTERFERENCE
	284.325	9.306	5	0.009306		233.527	82.845	20	0.082845
	284.984	2.203	500	0.002203		230.424	0.214	500	0.000214
Mn	257.611	0.284	500	0.000284	Bi	223.061	173.656	100	0.173656
	259.373	14.964	20	0.014964		190.241	BDL	1000	NO INTERFERENCE
	260.569	0.194	500	0.000194		306.772	36.661	100	0.036661
	294.921	1.555	100	0.001555		222.825	BDL	1000	NO INTERFERENCE
Fe	403.076	0.747	100	0.000747	Pb	153.317	16.58	500	0.01658
	259.941	20.946	10	0.020946		143.683	22.786	500	0.022786
	238.204	3.941	10	0.003941		206.17	BDL	1000	NO INTERFERENCE
	239.562	5.078	10	0.005078		220.353	25620	20	25.62
	244.451	3117.97	20	3.11797		168.215	19.597	500	0.019597
	261.187	5.43	20	0.00543		167.153	18.251	500	0.018251
	262.567	BDL	1000	NO INTERFERENCE		172.68	21.598	500	0.021598
	262.829	93.947	50	0.093947		405.778	2.422	500	0.002422
	275.573	22.137	100	0.022137	Li	283.305	9.322	500	0.009322
	241.331	14.022	100	0.014022		261.418	8.121	100	0.008121
	373.486	BDL	1000	NO INTERFERENCE		670.78	BDL	1000	NO INTERFERENCE
	228.616	BDL	1000	NO INTERFERENCE		460.289	BDL	1000	NO INTERFERENCE
Co	238.892	0.762	500	0.000762		323.261	BDL	1000	NO INTERFERENCE
	230.786	BDL	1000	NO INTERFERENCE		274.118	524.647	100	0.524647
	237.862	BDL	1000	NO INTERFERENCE					

TABLE IV (cont'd.)

TABLE IV (cont'd.)
Spectral Interference of Nb on Different Analytical Lines of The Elements

	Analytical Line (nm)	Contri- bution From 1000 ppm Nb	Toler- ance Level (mg/L)	Correction Factor		Analytical Line (nm)	Contri- bution From 1000 ppm Nb	Toler- ance Level (mg/L)	Correction Factor
Ni	231.604	BDL	1000	NO INTERFERENCE	La	408.672	BDL	1000	NO INTERFERENCE
	221.648	BDL	1000	NO INTERFERENCE		333.749	BDL	1000	NO INTERFERENCE
	232.003	30.543	100	0.030543		379.478	BDL	1000	NO INTERFERENCE
	227.021	1177.4	20	1.1774		418.66	BDL	1000	NO INTERFERENCE
	174.828	25.449	500	0.025449		448.691	BDL	1000	NO INTERFERENCE
Cu	300.249	10.263	100	0.010263	Ce	413.765	0.296	100	0.000296
	341.476	BDL	1000	NO INTERFERENCE		413.38	BDL	1000	NO INTERFERENCE
	324.754	67.114	20	0.067114		393.373	BDL	1000	NO INTERFERENCE
	327.396	9.97	200	0.00997		411.846	BDL	1000	NO INTERFERENCE
	224.7	39.334	100	0.039334		417.939	BDL	1000	NO INTERFERENCE
Zn	219.226	12.436	100	0.012436	Pr	422.535	BDL	1000	NO INTERFERENCE
	219.958	28.782	20	0.028782		414.311	0.276	100	0.000276
	213.856	BDL	1000	NO INTERFERENCE		401.225	1.483	50	0.001483
	206.2	BDL	1000	NO INTERFERENCE		430.358	BDL	1000	NO INTERFERENCE
	202.613	6.174	50	0.006174		406.109	0.203	100	0.000203
Ag	334.502	24.767	100	0.024767	Nd	417.731	BDL	1000	NO INTERFERENCE
	328.068	BDL	1000	NO INTERFERENCE		359.26	BDL	1000	NO INTERFERENCE
	338.289	0.426	500	0.000426		442.434	BDL	1000	NO INTERFERENCE
	224.641	812.777	20	0.812777		428.079	BDL	1000	NO INTERFERENCE
	243.779	0.758	500	0.000758		360.428	BDL	1000	NO INTERFERENCE
Cd	214.438	1.041	100	0.001041	Eu	420.505	0.018	100	0.000018
	226.502	1.731	500	0.001731		381.967	BDL	1000	NO INTERFERENCE
	228.802	0.869	500	0.000869		393.048	BDL	1000	NO INTERFERENCE
	361.051	BDL	1000	NO INTERFERENCE		390.71	BDL	1000	NO INTERFERENCE
	141.444	18.845	500	0.018845	Gd	342.247	0.72	100	0.00072
Ga	417.206	BDL	1000	NO INTERFERENCE		335.047	0.217	500	0.000217
	294.364	5.507	500	0.005507		336.223	5.214	0.1	0.005214
	287.424	44.556	100	0.044556		335.862	7.148	50	0.007148
	230.606	BDL	1000	NO INTERFERENCE	Dy	353.17	BDL	1000	NO INTERFERENCE
In	325.609	8.495	100	0.008495		394.468	BDL	1000	NO INTERFERENCE
	451.131	BDL	1000	NO INTERFERENCE		340.78	0.418	100	0.000418
	303.936	6186.35	10	6.18635		353.602	0.018	500	0.000018
						364.54	0.032	100	0.000032
					Lu	261.542	3.333	500	0.003333
						291.139	157.447	50	0.157447
						307.76	9.801	100	0.009801
						219.554	110.51	100	0.11051

Preferential Separation of Zr Without Loss of Analytes

For the efficient separation of Zr, three extractants, i.e., tri-n-butyl phosphate (TBP), di-n-hexyl octanamide (DHOA), and tri-n-octyl phosphine oxide (TOPO) were selected. A 1.1 M concentration of each ligand was used for the preferential separation of Zr. The extraction profiles were established at different aqueous feed acidity ranging from 0.01 M HNO_3 to 6 M HNO_3 (Figure 1). The D_{Zr} value was found to increase with an increase in aqueous feed acidity up to 3 M HNO_3 with a D_{Zr} value of 4, 3, and 1.9 for TOPO, TBP, and DHOA, respectively. This initial increase in D values with an increase in aqueous feed acidity can be attributed to the participation of the nitrate ion during complexation. Beyond 3 M HNO_3 , this drastic enhancement was found to be destroyed due to the competition of the H^+ ion with Zr^{4+} . The trend in D_{Zr} values using these three ligands can be explained on the basis of their electron donating ability. Based on this investigation, the aqueous feed acidity for processing of the actual Zr-Nb samples was optimized as 3 M HNO_3 .

Since the above study revealed that all of these ligands can be used for the efficient extraction of Zr, it also requires to know the fate of the analytes while processing with these solvent systems. Based on the analytical performance of different analytical lines of the elements and the spectral interference of Zr and Nb, the lines of Al 394.401 nm, B 182.641 nm, Ba 455.404 nm, Bi 206.170 nm, Ca 393.366 nm, Cd 226.502 nm, Ce 413.760 nm, Ga 417.206 nm, Gd 342.247 nm, In 451.131 nm, K 766.491 nm, La 408.672 nm, Li 670.780 nm, Lu 307.760 nm, Mg 279.553 nm, Mn 257.611 nm, Na 588.995 nm, Co 228.616 nm, Cr 205.618 nm, Cu 219.958 nm, Dy 353.170 nm, Eu 390.710 nm, Fe 373.486 nm,

Fig. 1. The distribution ratio values for Zr at different aqueous feed acidity.

Nd 430.358 nm, Ni 231.604 nm, Pb 405.778 nm, Pr 417.939 nm, Sm 359.260 nm, Sr 421.556 nm, Tl 190.864 nm, and Zn 213.856 nm are suitable for their determination in a Zr-Nb matrix.

Determination of Number of Contacts

One contact of the organic phase containing a ligand in dodecane was not sufficient to bring the Zr level to below the tolerance level of the specified analytical lines. Starting from 10,000 mg L^{-1} concentration of Zr, the separation process was carried out with equal volume of the organic phase. After each contact, the raffinate was analyzed for residual Zr. In most cases the tolerance level for Zr and Nb was above 100 mg L^{-1} (except the Zr tolerance for Ag 338.289 nm, Ba 455.404 nm, Mg 279.553 nm, Mn 257.611 nm; and the tolerance level of Nb on Mg 279.553 nm and Dy 353.170 nm). Hence, no contact of the organic phase will be decided based on this. It was observed that after four contacts of TOPO and TBP, the Zr concentration was brought down to less than 100 mg L^{-1} , while for DHOA six

such contacts were necessary. For Ag, Ba, Mg, and Mn, the correction factors need to be incorporated whenever necessary. The residual Zr after each contact of organic phase is summarized in Table V. In most cases, the spectral interference of Nb is very negligible as the initial amount of Nb in the sample is only 10%.

A similar exercise was carried out for Nb to understand its fate after each contact of the organic phase. The initial concentration of Nb was kept at 1000 mg L^{-1} since only 10% Nb was expected to be present. For all of these extractants, five contacts were found to bring the Nb concentration to below 100 mg L^{-1} . Table VI shows the residual Nb in the aqueous phase after each contact.

Analysis of Synthetic Samples

Synthetic samples were prepared with the composition Zr-10% Nb. Then the sample was processed with 1.1 M of ligand (TBP, DHOA, TOPO) in dodecane separately (five contacts for TBP and TOPO, but six contacts of DHOA). Then the raffinate was directly analyzed for the common

TABLE V
The Residual Zr After Each Contact
of Organic Phase With Phase Ratio 1

No of Contacts	TOPO (mg L ⁻¹)	TBP (mg L ⁻¹)	DHOA (mg L ⁻¹)
Initial	10,000	10,000	10,000
1	2500 ± 20	3333±29	5555±33
2	555±11	925±16	2777±21
3	115±8	237±9	1111±13
4	23.1±1.7	59.3±4.4	444±9
5	4.62±0.29	14.8±0.7	158±8
6	0.92±0.03	3.70±0.19	56.6±3.3
7	0.18±0.01	0.92±0.04	20.2±0.8

metallic constituents. The analytical results are summarized in Table VII. This study revealed that though TOPO was found to be the most efficient extractant compared to the other two ligands, the chemical separation of the matrix using this ligand led to the loss of analytes at trace level. Therefore, TOPO cannot be used for the determination of analytes at the 1 mg L⁻¹ level in a Zr-10% Nb matrix. Both TBP and DHOA were found to be successful for the determination of Ag, B, Ba, Bi, Ca, Cd, Ce, Ga, Gd, In, K, La, Li, Lu, Mg, Mn, Na, Co, Cr, Cu, Dy, Eu, Fe, Nd, Ni, Pb, Pr, Sm, Sr, Tl, and Zn at the 1 mg L⁻¹ level in Zr-10% Nb. Since the extraction efficiency for TBP was found to be more than that of DHOA, a lesser number of contacts of organic phase was required. Therefore, five contacts of 1.1 M TBP in dodecane are considered best for preferential chemical separation of Zr, followed by analysis of the raffinate for trace constituents.

CONCLUSION

A simple methodology was developed for the determination of ~30 analytes, including common metallic constituents and rare earth elements, at trace levels in Zr-Nb alloy. A systematic study was car-

ried out to identify the analytical lines of the elements having least spectral interference from Zr as well as Nb, while still providing sufficiently good analytical performance. TBP, DHOA, and TOPO were used for optimization of the chemical separation of these major matrix elements of Zr and Nb. Five contacts were found to be sufficient to bring down the Zr as well as Nb level below the tolerance level for TBP and TOPO, while six contacts of DHOA were found to be necessary to serve the purpose. Though TOPO showed the highest efficiency of Zr extraction, it cannot be successfully used for analytical purposes. It was observed that there was loss of a significant amount of constituents by using TOPO as the extractant. Both TBP and DHOA can be used for the trace level determination (at the 1 mg L⁻¹ level) of the analytes in a Zr-Nb matrix. Since DHOA needs more numbers of contacts which leads to the generation of more organic waste, TBP is the preferred for the present study.

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TABLE VI
The Residual Nb After Each Contact
of Organic Phase With Phase Ratio 1

No of Contacts	TOPO (mg L ⁻¹)	TBP (mg L ⁻¹)	DHOA (mg L ⁻¹)
Initial	1000	1000	1000
1	666.667	714.286	833.333
2	416.667	476.19	555.556
3	231.481	264.55	308.642
4	121.832	125.976	162.443
5	60.9162	59.9887	85.4964
6	24.3665	28.5661	44.9981
7	9.74659	13.6029	23.6832

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TABLE VII
Analytical Results for Synthetic Samples of Zr-10% Nb

Elements	Analytical Line (nm)	Initial (mg L ⁻¹)	TBP (mg L ⁻¹)	TOPO (mg L ⁻¹)	DHOA (mg L ⁻¹)
Ag	338.289	1	0.95±0.04	0.90±0.03	0.98±0.03
Al	394.401	1	0.97±0.05	0.93±0.04	0.97±0.04
B	182.641	1	1.03±0.04	0.95±0.04	0.97±0.03
Ba	455.404	1	1.02±0.03	0.85±0.04	0.95±0.04
Bi	206.170	1	0.96±0.05	0.90±0.04	1.03±0.05
Ca	393.366	1	0.97±0.03	0.87±0.04	1.01±0.04
Cd	226.502	1	1.05±0.05	0.98±0.03	0.98±0.03
Ce	413.76	1	0.95±0.03	0.76±0.04	0.99±0.04
Ga	417.206	1	0.98±0.04	0.95±0.04	0.96±0.05
Gd	342.247	1	0.96±0.05	0.79±0.04	1.02±0.06
In	451.131	1	0.99±0.04	0.96±0.05	1.03±0.05
K	766.491	1	0.99±0.03	1.00±0.04	1.00±0.04
La	408.672	1	0.97±0.05	0.82±0.05	1.02±0.04
Li	670.78	1	0.98±0.04	0.99±0.05	0.99±0.04
Lu	307.76	1	0.98±0.03	0.74±0.05	0.97±0.05
Mg	279.553	1	0.95±0.03	0.95±0.05	0.97±0.04
Mn	257.611	1	0.95±0.04	0.96±0.05	0.98±0.05
Na	588.995	1	0.98±0.04	0.99±0.05	0.98±0.05
Co	228.616	1	0.98±0.03	0.95±0.04	0.99±0.05
Cr	205.618	1	0.96±0.03	0.90±0.04	0.99±0.05
Cu	219.958	1	0.96±0.04	0.91±0.04	0.99±0.05
Dy	353.17	1	0.98±0.04	0.77±0.04	1.03±0.05
Eu	390.71	1	0.95±0.04	0.75±0.05	1.02±0.05
Fe	373.486	1	1.03±0.03	0.80±0.04	0.96±0.04
Nb	430.358	1	1.02±0.04	0.92±0.05	0.98±0.05
Ni	231.604	1	1.00±0.05	0.97±0.04	0.99±0.04
Pb	405.778	1	0.99±0.05	0.96±0.05	1.03±0.04
Pr	417.939	1	0.99±0.02	0.72±0.05	1.04±0.05
Sm	359.26	1	1.01±0.03	0.75±0.04	0.96±0.05
Sr	421.556	1	1.04±0.05	0.93±0.05	0.98±0.05
Tl	190.864	1	1.01±0.05	0.95±0.04	0.99±0.04
Zn	213.856	1	1.02±0.05	0.90±0.06	0.99±0.03

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